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BARC STUDIES IN COLD FUSION

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BARC Studies in Cold Fusion

Cold Fusion Experiments at Hall No.2 : Experimental Results of Heavy Water Electrolysis using a Commercial Pd–Ni Electrolyser

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INTRODUCTION :

When the news about the occurrence of cold fusion broke–out[1,2], it was decided to conduct similar experiments at Heavy Water Division, BARC in collaboration with Neutron Physics Division. Due to the urgency of the work it was felt necessary to employ a readily available electrolyzer with minimum modification so as not to waste minimum time in setting up of the experiments. Fortunately, a commercial laboratory hydrogen generator was available in a ready to use condition. It was therefore decided to conduct the initial experiments with this electrolyzer. Both neutron and tritium measurements ere carried out. This paper gives a detailed account of these experiments and the results obtained are discussed.

The Electrolyzer :

The electrolyzer employed was a commercially available diffusion type ultrapure electrolytic hydrogen generator. A schematic sketch of the electrolytic cell is shown in Fig.1a. The anode is of Nickel and the cathode consists of specially activated palladium membrane tubes. These anodes and cathodes are mounted as shown in Fig.1b. The outer nickel body of the cell and a central nickel tube serve as coaxial anodes and sixteen cathode tubes are mounted with the help of PTFE spacers in between these two anodes as shown in Fig.1b. All the cathode tubes are sealed at the top and are opening into a small reservoir through which the deuterium comes out. (Fig.1a). Some typical cell parameters are listed in Table (1). During electrolysis the oxygen generated at the anode is vented through a series of plates (for draining any alkali carryover) through a vent tube at the top. The hydrogen ions which deposit at the Pd cathodes, under the influence of applied electric potential diffuse through the walls of the tubes. These ions recombine inside the tubes to form molecule deuterium. The electrolyte level in the electrolytic cell is maintained via remote reservoir of water. The unit is completely automatic and is equipped with pressure control, a solenoid valve, electrolyte leak detector, low water level detector, temperature control etc.

Detectors :

Initially a plastic scintillation detector with PM tube ( ) and an assembly of four BF_3 detectors were used for radiation monitoring. Subsequently He3 detectors were also employed.

Experimental :

To start with, the electrolyzer was operated with 20% NaOH in natural water as the electrolyte as a blank run. A BF_3 counter (efficiency $\sim 10^{-4}$) and plastic scintillator counter (efficiency $\sim 10^{-2}$) were kept about 10 cm from the cell. This operation was carried out for about 48 hr for collecting the background data. The cell was then drained of its electrolyte flushed with heavy water and then filled with 20% NaOD solution in D_2O (>99.8% isotopic purity) and was operated initially at 30 amps. The current was slowly raised to 60 amps corresponding to a current density of 200 mA/cm2. After an operation under these conditions for about 3 hrs both the neutron counters started showing occasional rise in the neutron counts and after about 5 hrs of operation both the counters suddenly showed two very large peaks and at the time of the second peak the current is the electrolyzer suddenly increased to ~120 amps on its own and the electrolyzer immediately got tripped. Later it was found that the plastic insulation of the electric wire between the DC power supply and the electrolyzer had melted and even the soldering at the connection had melted. The diodes of the power supply had burnt and that is why the unit had tripped. The results of the neutron measurements of this run are shown in Fig.2. The total number of neutrons produced is 10^8 over a period of several hours of electrolysis, however actual neutron emission was in bursts of 5 minutes and 9 such bursts were observed. During this operation no tritium analysis was carried out but at the end of the run the electrolyte was analyzed for its tritium content by liquid scintillation counting and was found to contain 1.5 μci/ml tritium activity. The tritium activity of the heavy water used for preparing the electrolyte was 0.075 nci/ml. As discussed later this tritium build up is much more than what can be accounted for by the electrolytic enrichment.

The cell was drained of its electrolyte and flushed with heavy water many times for decontaminate from tritium. Finally the electrolyte solution was prepared using heavy water containing 0.075 nci/ml tritium and the electrolyzer charged with this solution and left overnight. Next day this electrolyte was analyzed for its tritium content and now electrolysis was started using an external power supply, as built in power supply of the electrolyzer had got damaged.

The electrolyzer was operated at currents of 60–62 amps (current density ~200 mA cm–2) continuously for 54.5 hrs. Samples of electrolyte were with drawn at different time intervals during this operation for tritium analysis. During this run no significant neutron peak was observed in any of the detectors.

The tritium content of the electrolyte also did not increase, instead it decreased from 0.32 nci/ml (at 0 hrs) to 0.12 nci/ml at the end of the run. This decrease can be explained easily. The starting sample showed higher tritium content than the D2O employed because of the residual tritium in the electrolyzer from the previous run. Now as the electrolysis proceeded D2O of low activity (0.075 nci/ml) was used for continuously maintaining the level of the electrolyte which was therefore diluting the tritium in the electrolyte. At the end of this run, through the current had been put off, the neutron detectors were still kept on looking at the cell. Nothing happened for the next 30 hrs. Even the tritium content of the sample withdrawn about 24 hrs after putting off the current showed same reading. But about 30 hrs after putting off the current a large neutron burst was observed. Corresponding to about 10^6 neutrons. As this neutron peak occurred during night, next morning another sample of electrolyte was withdrawn and analyzed for its tritium content. It was found to contain 121 nci/ml tritium. The experiment was stopped at this point but the electrolyser was left as such with the electrolyte in the cell and deuterium at 1 kg/cm2 in its deuterium chamber. After a lapse of about a month the electrolyte was removed and analyzed for tritium. A four fold increase in the tritium was observed. All these results of tritium and neutron measurements are depicted in Fig.3.

The electrolyzer has since been cleaned and is being charged with fresh electrolyte. Another operation of longer duration with online tritium counting both in deuterium gas and the electrolyte line is being arranged to establish a point to point correspondence between the neutron and tritium counting.

Discussion :

The results of the neutron and tritium measurements are tabulated in Table 2. The observed tritium concentrations have been corrected for the tritium enriched due to electrolytic separation of deuterium and tritium and evaporation. In the last two columns of this table the probability of cold fusion occurring via neutron and tritium channel have been listed for both the cases. These have been calculated in terms of the no. of particles (neutron or Tritium) being.produced per pair of deuterium atoms absorbed in the metal. A Pd : D ratio of 0.6 has been taken as widely reported in the literature. It is quite important to note from this table that the tritium channel seems to be much more probable than the neutron channel through in 'Hot Fusion' their probability is equal. One point which needs further experimental confirmation is that both the channels seen to be occurring simultaneously because as mentioned earlier in the second run no neutron and tritium peak was observed for a long duration but the tritium content of the electrolyte was found to have increased multifolds after a neutron burst was noticed. As already mentioned this needs further confirmation which can be done by on line measurement of tritium which is being attempted by us at present. Another interesting observation is that electrolysis seems to be necessary only for loading the metal with deuterium. A flowing current does not seen to be a necessary condition for fusion to occur as is clear from the observation in RUN2 of the electrolyzer where both neutron peaks and tritium were recorded only about 30 hrs after the current had been put off. A four fold increase in tritium over a period of is one month further strengthens this view point. Observation of tritium in Pd loaded directly from gas phase also substantiated the conclusion that ongoing electrolysis is not really essential on cold fusion to occur. Another observation from this work is that the Pd metal seems to lose its capability to produce cold fusion with time. As can be seen from a comparison of RUN1 and RUN2 in the latter the no. of neutrons and tritium produced seen to have decreased. This observation is very important and calls for further investigation in terms of some specific parameter(s) of the metal which is important for cold fusion. A multi dimensional characterization including lattice structure etc of fresh and spent electrodes will go a long way in understanding this phenomena and will also probably throw some light on the mechanism of 'Cold Fusion'.

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The authors have been getting unstinted cooperation from several scientists in various aspects of these experiments. They are extremely thankful to each and every one of them. They include SS C.K. Pushpangathan, V.H. Patil, Arun Kumar and N.P Sethuram of Heavy Water Division and Shri R.K. Rout Kum V. Chitra and Shri L.V. Kulkarni of Neutron Physics Division. The all important tritium measurements were carried out by Dr T.S. Iyengar painstakingly, which is gratefully acknowledged. Shri H.K. Sadhukhan, Head Heavy Water Division has contributed immensely by fruitful discussion and authors are thankful to him.

References:

1) M. Fleischmann, S. Pons; J. Electranal. Chem. and Interfacial Electrchem.; 261; 301–308; 1989
2) S.E. Jones et al; Nature; 338; 737; 1989

TABLE 1

Details of Electrolytic Cell

Vol. of Pd cathode = 19.98 cm^3
Wt. of Pd = 247.95 gm
Area of cathode = 300 cm^2
Current = 60 amps
Current density = ~ 200 mA/cm^2
Electrolyte = 20% NaOD in D_2O
Total vol. of electrolyte = 250 ml

TABLE 2

Summary of Neutron and Tritium Yields
(current density = 200 mA/cm^2)

Duration of	Total no. of	gm atoms of	
	Electrolysis	neutron in Bursts	Tritium
Run 1 21.4.89	72 hrs.		1.3×10^{-8}
Run 2 16.6.89	54 hrs.		$^{*}1.0 \times 10^{-9}$ $^{*}3.9 \times 10^{-9}$

* These were obtained 30 hrs. and 27 days respectively after the current had been switched off.

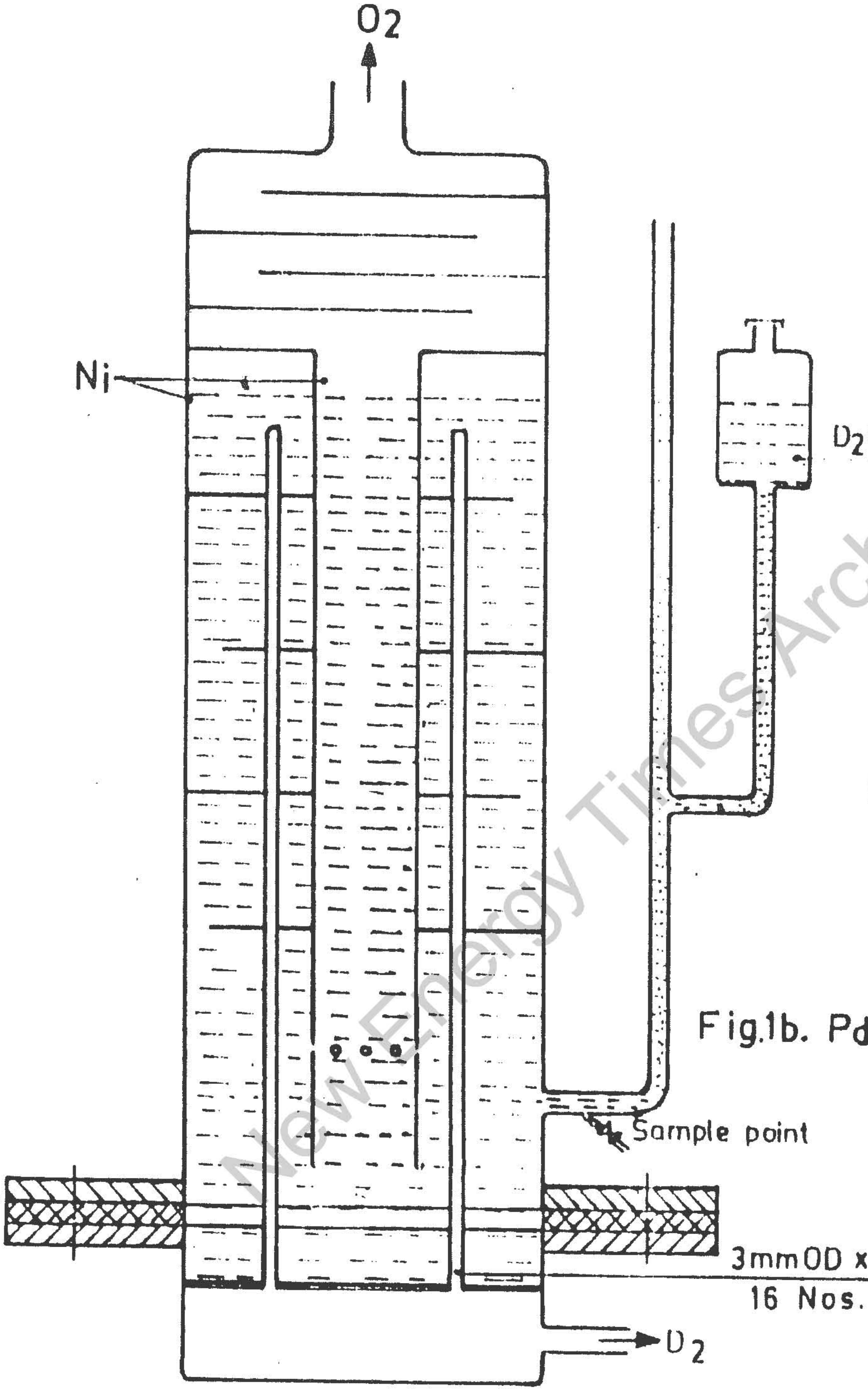

Fig.1a. Electrolytic Cell.

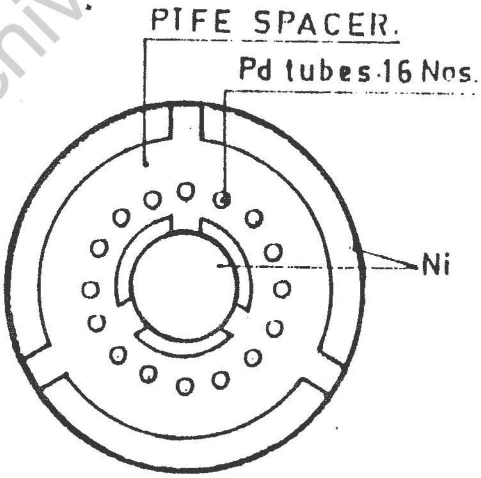

Fig.1b. Pd tube arrangement.

HWD/msk/pilla) 27.8.89

Electrolyser Systems used for Cold Fusion Studies

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The electrolytic cells and cell modules including complete electrolyser system were fabricated and provided by Desalination Division, Hydrogen Section, for the cold fusion studies carried out in collaborative work by Heavy Water Division, Neutron Physics Division and Desalination Division.

Two types of cell configurations were used in the studies. A single cell monopolar titanium electrode assembly and a bipolar multicell module consisting of Palladium – 25% silver alloy cathodes were fabricated.

Single cell titanium system

This cell consists of a tubular configuration with a central solid titanium rod forming the cathode and the concentric titanium outer tube functioning as anode. The current supply to the electrodes were provided by insulated flanged and connections which were also used to assemble the cell. The cell itself was housed inside a stainless steel tubular jacket with provision for electrolyte inlet and product gas outflow. The gas generated between the electrodes gives a bouyant force to keep the electrolyte in circulation so that an uniform temperature of the electrolyte could be maintained. The product gas mixture, consisting of Deuterium and oxygen, coming out of the cell was brunt in a burner condenser and the product heavy water formed was returned into the cell, thus forming an invariant closed circuit cell system. Two identical cells were provided so that one of the cell could be operated simultaneously with light water, generating hydrogen and served as a reference to the other cell operating with heavy water.

Multicell module assembly

A five cell module of bipolar filter press configuration having Palladium – Silver alloy as cathodes and porous nickel as anodes was fabricated using 0.1 mm thick 25% Ag–P4 alloy sheets. The electrodes were of circular geometry with an electrode area of 100 Cm^2. The cell module could be operated even upto a high current density of 1 A/Cm^2 and temperatures of 100^0 C. The module consists of 5 cells connected in series and the mixed gaseous product was carried out of the cell module by the recirculated electrolyte.

Electrolysis system

The two types of cell configurations are so constructed that they can be fixed into a circulating closed loop electrolyse unit for long term continuous operation. This will enable to study the accumulation of fusion products like tritium and helium after sufficiently long hours of continuous operation.

At integrated 5 cell module electrolyser system was fabricated and the same was operated on a continuous basis for detection of cold fusion Phenomena in Palladium matrix. The electrolyser consists of a closed loop wherein the product heavy water formed by burning of deuterium in the burner condenser could be recycled back to the electrolyser. Fig.1 gives a schematic flow diagram of the electrolyser system used in the cold fusion studies conducted in early experiments.

D.C. power is supplied to the cell module. The product gases viz. deuterium and oxygen, are carried along with the electrolyte ;to a vertical tube type gas–liquid separator. No separate circulating pump is used. The continuous generation of gases between the electrodes and the consequent gas lift is used for the circulation of the electrolyte through the system. The hot electrolyte gas mixture is cooled in an electrolyte cooler to maintain a steady and desired operating temperature. Thermowells are provided before and after the cell module to measure the temperature rise across the module during operation. The electrolyte after separation of product gases returns to the cell module by gravity. The gas mixture leaving from the gas liquid separator is passed through a D_2O scrubber to remove any NaOD carryover. It is again passed through a bubbler which also acts as a flash back arrester. The gas entering the burner–condenser is lit by an electrical spark mechanism and a spark detector is used for ensuring a steady and continuous flame at the burner tip. The burner condenser is a double walled jacketted cylindrical vessel which is cooled by passing chilled water through the annular space. Additional cooling coil is also provided inside the vessel to sufficiently cool and completely condense all the heavy water formed by burning of deuterium. The product Heavy water from the burner condenser is put back into the electrolyser to form a closed electrolyte loop. Heavy water can be added to the system through a separate feed pump for make up when the system is in open loop operation. Process parameter like temperature, pressure, cell voltage and cell current are continuously measured and indicated in the front panel of the system.

Electrolysis operation for cold fusion detection studies

The electrolyser system with 5 cell bipolar filter press module having pd–Ag cathodes and porous nickel anodes was operated on a continuous basis during May '89. The cell operating temperature was maintained around 60 C and pressure at about 0.6 to 1.0 kg/Cm^2. The applied current density varied from 0.4 A/Cm^2 to 0.75 A/Cm^2 with a cell voltage of 12–15 volts. The unit was operated for a total of 75 hrs. Periodic addition of heavy water was carried out as open loop operation was resorted to and samples of heavy water from the burner condenser taken out on daily basis for tritium detection.

BARC Studies in Cold Fusion

Search for Electrochemically Catalysed Fusion of Deuterons in Metal Lattice

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Introduction

Recently, Fleischmann and Pons' have obtained evidence for the fusion of deuterons induced at low temperature, through the electrolysis of deuterium oxide at a palladium cathode. It is believed that this can be achieved if the deuterium loading of the lattice exceeds the value for PdD In view of the relevance of this problem to this Centre, a programme of work was initiated in this Division. This report is a summary of the behaviour of Pd and other metals during charging in alkaline heavy water.

Experimental

Materials, Reagents and Apparatus.

Electrodes of different metals were used. These include a hollow Pd cylinder (area 5.87 cm^2, thickness 0.4 mm), Pd ring (area .b 14.5Cm^2, thickness'2 mm), Pd foil (area 1.5 Cm^2, thickness 0.3 mm),Ti plate (area 8 cm^2,thickness 0.5 mm) and a triangular piece of Ni–Ti alloy of area 10 cm^2 and weight 10.5 gm. Platinum gauze, Pt disc or Pt foil of large area was used as the anode. Heavy water (99.87e purity)and pure Li metal were used to obtain 0.1 M LiOD. Iolar–2 N_2 or argOn was used for deoxygenation and stirring. All electrodes were lightly abraded with emery, rinsed with acetone and dried before use.

Electrolysis cells were made of quartz for the container and the lids were of PTFE or glass. Provisions and inlets for deoxygenation, addition and removal of solution and temperature measurement were made. Loss of D_20 due to evaporation and due to evaporation and electrolysis was compensated.

Equipments:

Galvanostatic sources and current pulsing units were made in the laboratory. A Digital Panel Meter (PLA, DM–20), was used for voltage measurements. Neutron counting and tritium activity studies were carried out, as described later. Set–up is shown in Fig.1.

Results:

1. Differential Enthalpimetric studies

Twin cells composed of Pd as cathode (5.9 Cm^2)and Pt as anode (gauze) in one cell was coupled in series with Pt as cathode (5.9 Cm^2)and Pt as anode (gauze) in another cell. The purpose was to assess the magnitude of heat effects due to reactions like deuterium adsorption on the electrode, its recombination, dissolution in the lattice,etc. The celis were insulated by Dewar and 45 ml of 0.1 M LiOD were taken in quartz cells. The temperatures were monitored by matched thermistors using a bridge circuit and also measured with thermometers. The temperature of the two cells during charging is shown in Fig.2. The temperature of Pt–Pt cell remained nearly constant whereas the temperature of Pd–Pt cell increased and attained a high value. The temperature rise in Cell I (Pd–Pt) is due to absorption, dissolution and interaction of deuterons in Pd lattice.

2. Calorimetric Measurements of Enthalpy changes.

A modified isoperibol solution calorimeter with an accurate thermistor bridge was used. The cell with contents were enclosed in a tight–fitting Dewar and was immersed in a thermostat at 250C for thermal insulation. Electrodes of hollow cylindrical Pd cathode(5.48 cm^2) and Pt sheet anode with 50 ml 0.1 N LiOD were used. Iolar–2argon was used for deoxygenation and the solution was stirred mechanically. Charging was effected at different current densities and the terminal voltage in each case was noted. The solution temperature was monitored by the thermistor probe and bridge and also by a sensitive thermometer. The temperature increase as a function of time at different c.d. is shown in Fig. 3. The heat capacity of. the cell and components was determined by electrical calibration and corrections for heat losses were applied on the basis of Newton's law of cooling (Fig.4). The results are included in Table 1.

3. Extended Electrolysis with Current Pulsing:

3.1 Cylinder Electrode : A hollow cylindrical Pd cathode (5.9 cm^2)and a Pt gauze anode were used and 0.1 N LiOD was electrolysed in a quartz cell with nitrogen bubbling. Initially, a constant current of lA was used and when the temperature reached 600C pulsing was commenced between 1 to 2A at 1 s. interval. The temperature was controlled to 63^{0}C by forced circulation of air. Neutron flux measurements were made and D_20 was added for2 was added for make up. After 41.8 hours during which 52.2 AH were consumed, the electrolysis was terminated. Measurement of tritium build–up in the final solution showed 3.75 μCi.

3.2 Ring Electrode :

(1) 65 ml of 0.1 N LiO,D in D_20 were electrolysed in a quartz cell using a Pd–ring cathode (14.5 cm^2) and two Pt discs as anode. At low current densities, the cell voltage was observed as a function of current and this is shown in Fig. 5. Later, electrolysis was carried out for4nine days with current pulsing between lA and 2A (80 h), 3A and 4A (20 h)and between 4A and 4.5 A (7 h) consuming a total of 296 Amp.hours. Neutron activity and capture 1; measurements were made throughout the duration of electrolysis. At the conclusion of the electrolysis, tritium content in the solution was found to be 16.25 μCi.

(2) The above experiment was repeated using 0.1 N NaOD and a total of 231Amp. hour were passed during 77 hours. Neutron counting and tritium activity measurements were carried out.

(3) The same ring electrode, after degassing in vacuum, was subjected to 844amp. hour charging in 382 h. in 65 ml of deaerated 0.1 N LiOD. There was no significant tritium build–up in solution. The electrode was greyish black in colour.

3.3 Ni–Ti Electrode:

A Ni–Ti cathode (10 cm^2) was used in 0.1 N LiOD and a total charge of 135 amp. hr were passed over 111 hrs. Appreciable neutron activity was observed. The cathode was observed to flake off and disintegrate in powder form.

3.4 Ti Electrode:

A Ti sheet cathode (8 Cm^2 area) and Pt sheet anode were used in the electrolysis of 1 M NaCl in D_20 at 34 mA.cm^{-2}. The terminal voltage was 4.4 V and temperature rose from 27^{0}C to 36.60C in 53 minutes. Prolonged electrolysis did not show any significant increase in temperature.

4. Nuclear Measurements:

Four different types of measurements were made to identify the emission of neutrons from the electrolysis cells.

1. Detection and direct measurement of neutrons were based on the use of He^3 detectors arranged in a well–counter as well as a Li^6 enriched scintillation detector (Bicron, Model NP–2). The detectors were calibrated by Am–Be source. Near complete rejection of high energy 1/–rays was ensured by proper discrimination of the 2.5 MeV Co^{60} sum peak using a Co^{60} source.
2. Detection of high energy capture –rays of Gd,Pt and Pd was achieved by using Ge(Li) or HPGe detectors.

3.Measurement of low energy capture –rays of energies 199, 944and 1186 KeV was carried out with a HPGe detector. 4. Gross counting of 1/–rays of energy greater than 3 MeV was effected by means of a properly shielded 3" x 3" NaI (II) detector.

All the above measurements were done in combination to yield t–cross–validatied results. However, in some cells, only a single type of measurement could be made.

Neutron counting was performed both in the MCS mode (using IBM–PC based 8 K MCA system) and in the PHA mode whenever possible. Different dwell times ranging from 0.5 sec. to 60 sec. were selected in the MCS mode to check whether neutron emission is continuous or in "bursts". The complete counting set up is given in Fig. 6. The results can be summarised as under:

a) Palladium hollow cylinder cathode (run 3.1)
The 1186 KeV gamma ray activity was measured every 100 sec. interval for more than 24 hours. In Fig.7, three definite 'spikes' can be identified. The duration of the 'bursts' was 14 to 20 minutes.
b) Palladium ring cell (run 3.2.1)A time correlated analysis of the neutron counts in the Li scintillation counter and measurement of r–rays of energy greater than 3 MeV in the NaI (Tl) detector were carried out (Fig.8). The correlation co–efficient for the 50 observations was 0.26 which is significant at the 5% level.
c) Ni–Ti cathode cell (run 3.3)Neutron counting was carried out using Hel as well as Li scintillation detectors with the former in both the MCS and integral modes and the latter in the MCS mode. The cell was run initially at 1A current and when the current was increased to 2 – 2.5 A, three well–defined "spikes" were registered in the MCS mode as shown in Fig.9.

The count rates of He and Li scintillator are not correlated in any significant manner, possibly because of the different efficiencies of detectors and geometries. However, tiny spikes are registered in the He detector.

d) Palladium ring cell (run 3.2.3)

Several spectra for the low energy capture gamma rays were detected using HPGe detector for durations from 10,000 to 50,000 seconds. In some spectra, 199, 944 and 1186 KeV capture could be identified though they were not traceable in other spectra. As the accumulated count rates for these energies are rather small, it appears that neutron emission is low and not continuous.

Discussion

Electrolysis of alkaline heavy water results in the splitting of D_20 with evolution of deuterium at the cathode and oxygen at the anode. The electrode process involves charge transfer, adsorption of the intermediates, subsequent reaction and gas evolution(2) On pd electrode,the discharge reaction in alkaline solution is followed by a rate determining recombination of adsorbed deuterium atoms at low over potential,whereas at high over potential an electrochemical desorption reaction is favoured. In the case of Ni–Ti, the discharge reaction is always accompanied by rate determining electrochemical desorption reaction.

The uptake of deuterium by metals during charging depends on the reaction

$$MD_{ads} \longrightarrow MD_{abs} \longrightarrow MD_{lattice} \qquad (1)$$

and is,therefore, governed by the fraction of the electrode surface covered by adsorbed D, solubility of deuterium in the metal and its diffusivity. The observed rise in temperature of the electrolyte is not due to the exothermic dissolution of deuterium in Pd, Ni–Ti and Ti or due to other chemical factors.

The measured overpotential is composed of ohmic, activation,adsorption, diffusion and concentration overpotential terms. The ohmic resistance and polarisation resistance cause Joule heating and thereby contribute to observed changes in enthalpy. Had the cell systems been Q–reversible, then if the polarisation is reversed, the electrode reactionsat Pd and Pt electrodes should also be reversed. In the upper limit the maximum Joule heating is the product of the cell voltage E and cell current i. In the case of Pd–Pt electrodes, the minimum voltage or back E.M.F for electrolysis of D_20 was calculated from thermodynamic data as 1.54 V. Therefore, the electrical power available for Joule heating is (E–1.54)i and this is the lower limit. The enthalpy changes calculated for different c.d. and the ratio of thermal output to the power input,expressed as per cent breakeven are also included in Table 1.

The predominant process during d.c. polarisation is the electrolysis of D 0 and has been checked by measuring the volume of D_2 and 0. mixture2 has been checked by measuring the volume of D_2 and 0. mixture liberated in a fixed electrolysis time using a precision integral flow–meter and by gas chromatographic analysis of the composition of the gasmixture. As excess heat is liberated over and above electrolysis, it is clear that some other reactions are responsible for the excess enthalpy observed. Pauling ' ' ascribed the excess heat to the formation of palladium deuteride. However, Bockris and coworkers. ' have shown that exothermic effects due to solution or D in Pd, recombination of D atoms, formation8 of D_20 etc.cannot account for the observed heat evolution. Normal chemical reactions cannot account for the generation of neutrons orthe production of tritium during charging Pd with deuterons. As has been pointed out by Fleischmann and Pons ' ', the results can be rationalised and understood on the basis of cold fusion reactions occurring between deuterons in the Pd lattice as indicated below:

$$ {}_1^2D + {}_1^2D \longrightarrow {}_1^3H + {}_1^1H \qquad (2)$$

$$ {}_1^2D + {}_1^2D \longrightarrow {}_2^3He + {}_0^1n \qquad (3)$$

In the present work, the emission of neutrons, reasonably above the background level, and the build up of significant tritium activity in excess of the blank value, have been confirmed in four different electrolysis experiments. In certain experiments neither the evidence for significant neutron emission nor any appreciable build up of tritium activity has been observed. It is likely that in such cases charging was not sufficient for ensuring optimum loading of the lattice with deuterons for inducing fusion. However, it appears that in addition to reaction channels (2) and (3), the possible occurrence of a non–emitting nuclear process cannot be precluded. This reaction can be written as

$$ Pd + {}_1^2D + {}_1^2D \xrightarrow[\text{catalysed}]{\text{lattice}} {}_2^4He + Pd^* \qquad (4)$$

which implies that the lattice is excited to a higher energy level to conserve both momentum and energy. It is likely that during the subsequent lattice relaxation, the excess energy stored in the lattice is liberated as heat(5) This mechanism would lead to the formatiOn and build up of He inside the metal and can possibly account for the observed low yield of neutrons or tritium in certain experiments. Accurate mass spectroscopic3/He4 ratiO in the cathode material is needed to substantiate analysis of He/He4 ratiO in the cathode material is needed to substantiate9this view. In conclusion, it is necessary to examine in detail the different parameters and optimise important factors like metallurgical history and pre treatment of the cathode, solution chemistry, surface chemistry and electrochemistry to achieve reproducible fusion throughelectrochemical charging of metals in heavy water.

Acknowledgements

Authors are grateful Lo Dr.R.M.Iyer, Director, Chemical Group for his keen interest and encouragement. Acknowledgements are due to Shri T.S.Murthy, Director, Isotope Group for kindly providing the data on tritium analysis. Support from Shri S.P.Chaganty of Electronics Division for scintillation detector and associated electronics facility,Shri J.D.Gupta and Ms Suman Kumari of Computer Division for the 8KPC–based MCA system and Dr. M.R.Iyer of Health Physics Division for 3well–counter and a MCS mode acquisition set up are gratefully He^3 well–counter and a MCS mode acquisition set up are gratefully acknowledged. In particular, we wish to acknowledge the painstaking efforts and support of the following scientists of the Division in providing the reliable data cited in this work.

1.Continuous nuclear data acquisition – Ms G.Leela, Ss. Sanjeevkumar, Sunil Jai Kumar, Rakesh Verma, Anna John, D.Shreevalsan NairQ.,and S.C.Hodawadekar.
2. Nuclear and electrochemical instrumentation – Ss. K.C.Thomas,J.R.Kale, R.G.Dalavi and A.W.Sahani.
3. Calorimetric measurements – Shri S.S.Sawant.

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Table 1

Excess enthalpy generated during electrolysis of LiOD
Area of Pd hollow cylinder : 5.48 cm², Temp . 25ºC.

Current density $mA.cm^{-2}$	Energy input iE Watts	ΔH, measured Watts	Excess enthalpy (in % breakeven)	
			$\frac{\Delta H \text{ measured}}{(E-1.54)i} \times 100$	$\frac{\Delta H \text{ measured}}{Ei} \times 100$
36	1.25	1.00	105	80
73	3.96	3.13	94	79
110	7.30	5.60	88	77
146	10.47	6.95	75	66
183	15.46	10.79	78	70

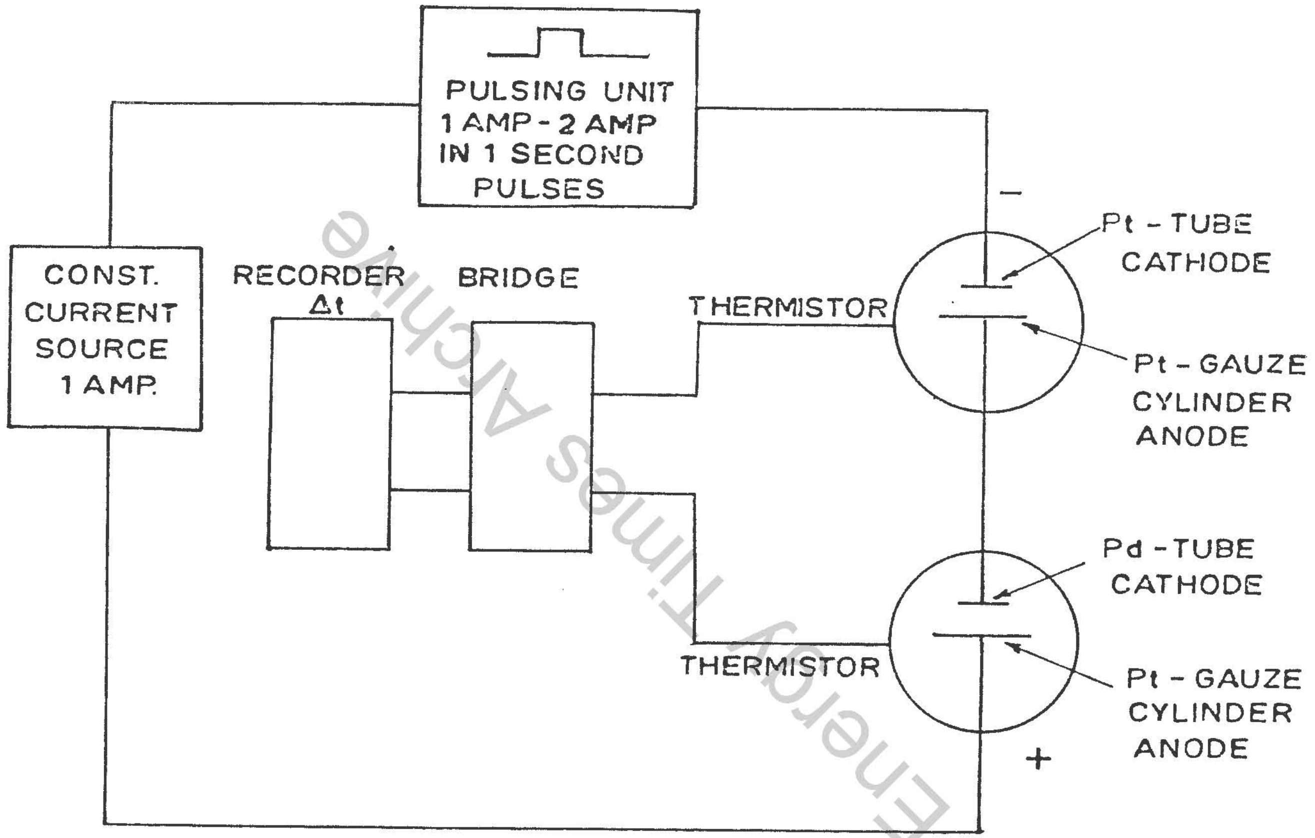


FIG. 1 EXPERIMENTAL SET - UP

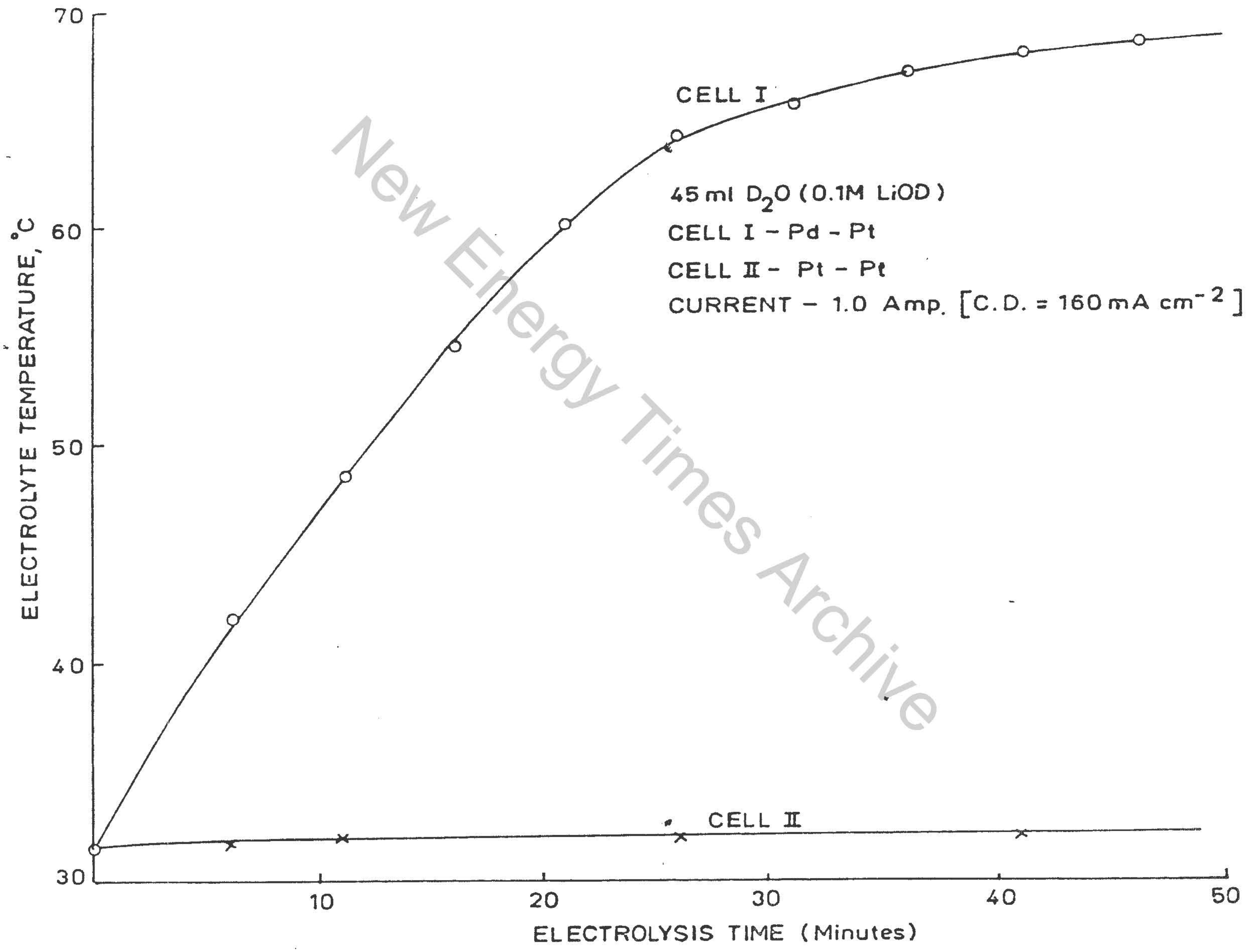


FIG. 2 DEPENDENCE OF TEMPERATURE ON TIME

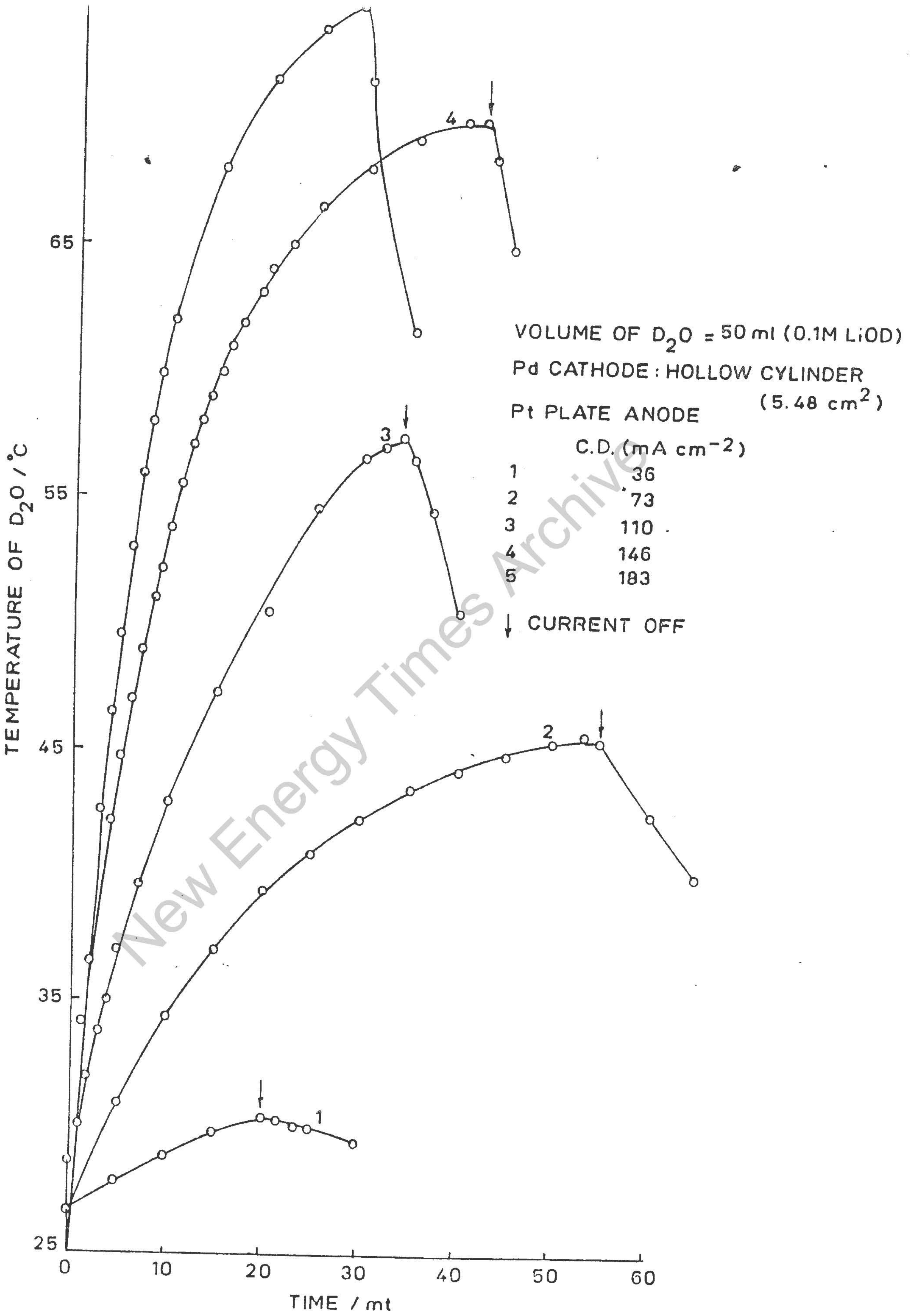


FIG. 3 TEMPERATURE CHANGES DURING CHARGING

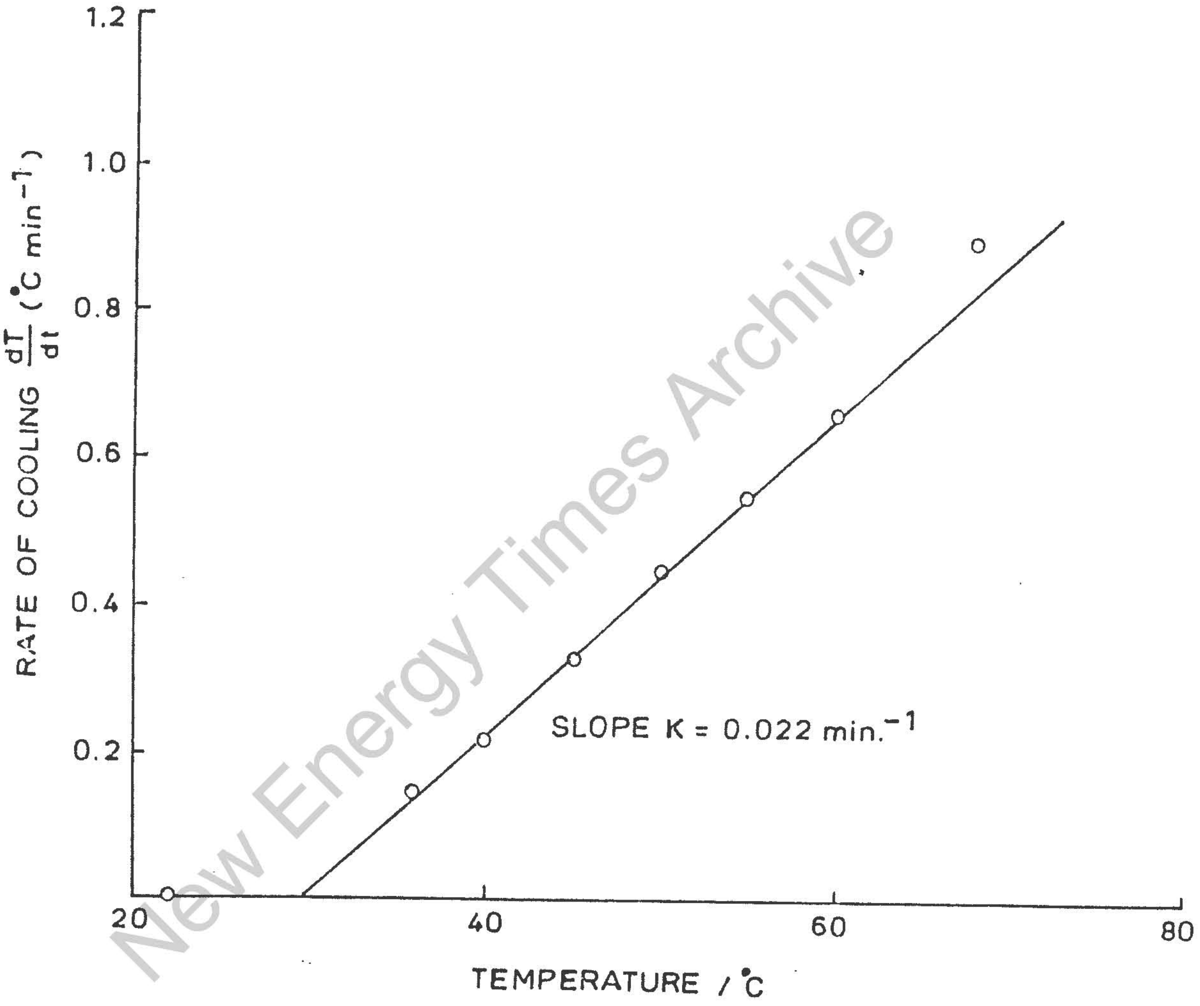


FIG. 4 TEMPERATURE-RATE OF COOLING, RELATIONSHIP

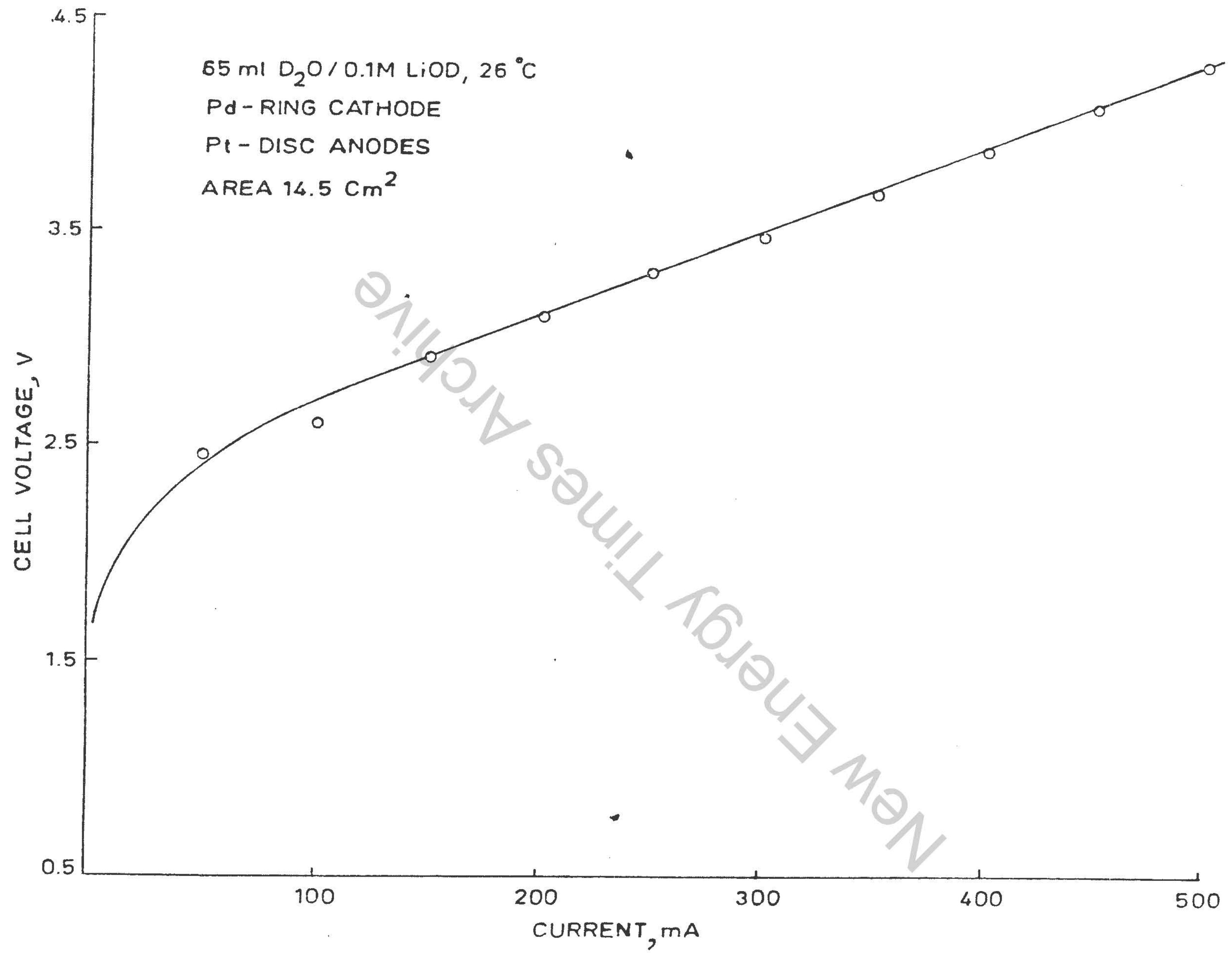


FIG. 5 CELL TERMINAL VOLTAGE AS A FUNCTION OF CELL CURRENT

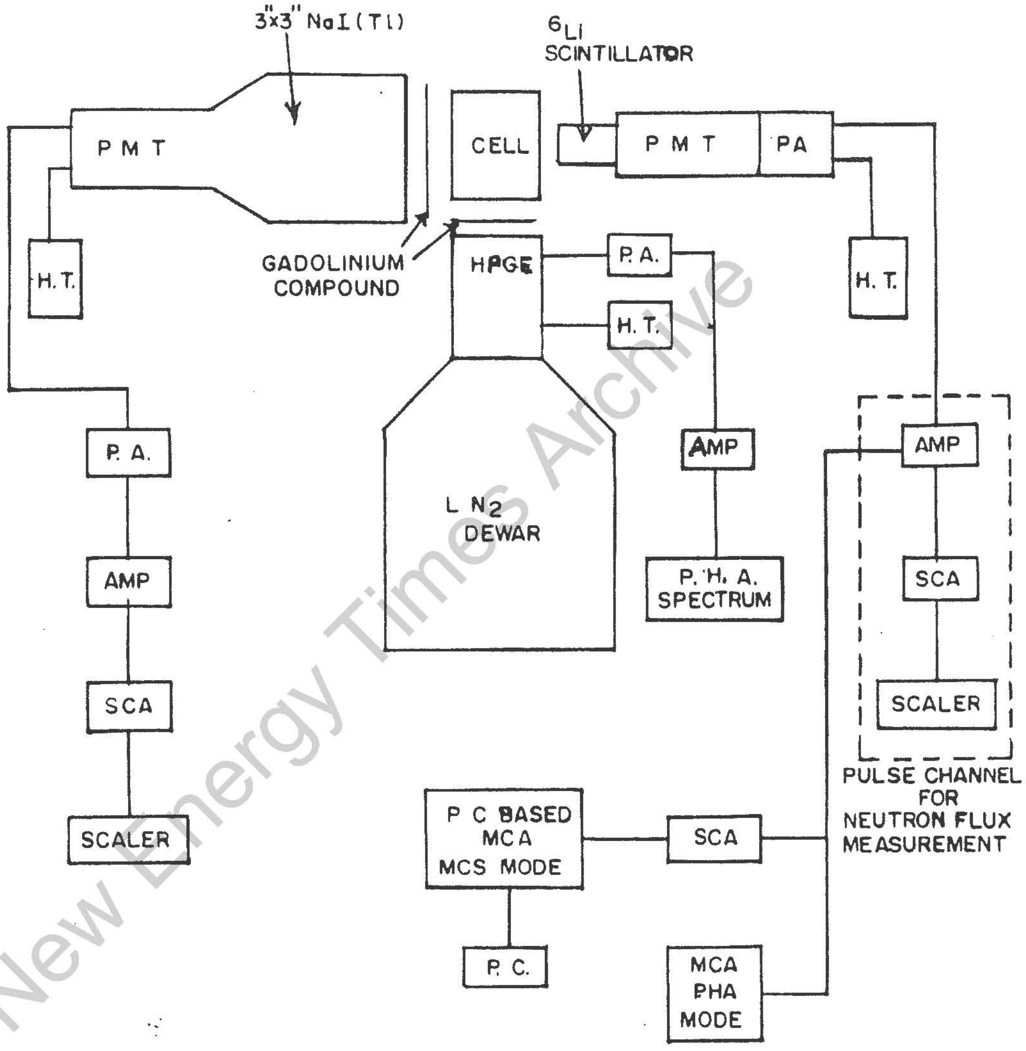


FIG. 6. COUTING SET-UP FOR NEUTRONS AND GAMMA RAYS.

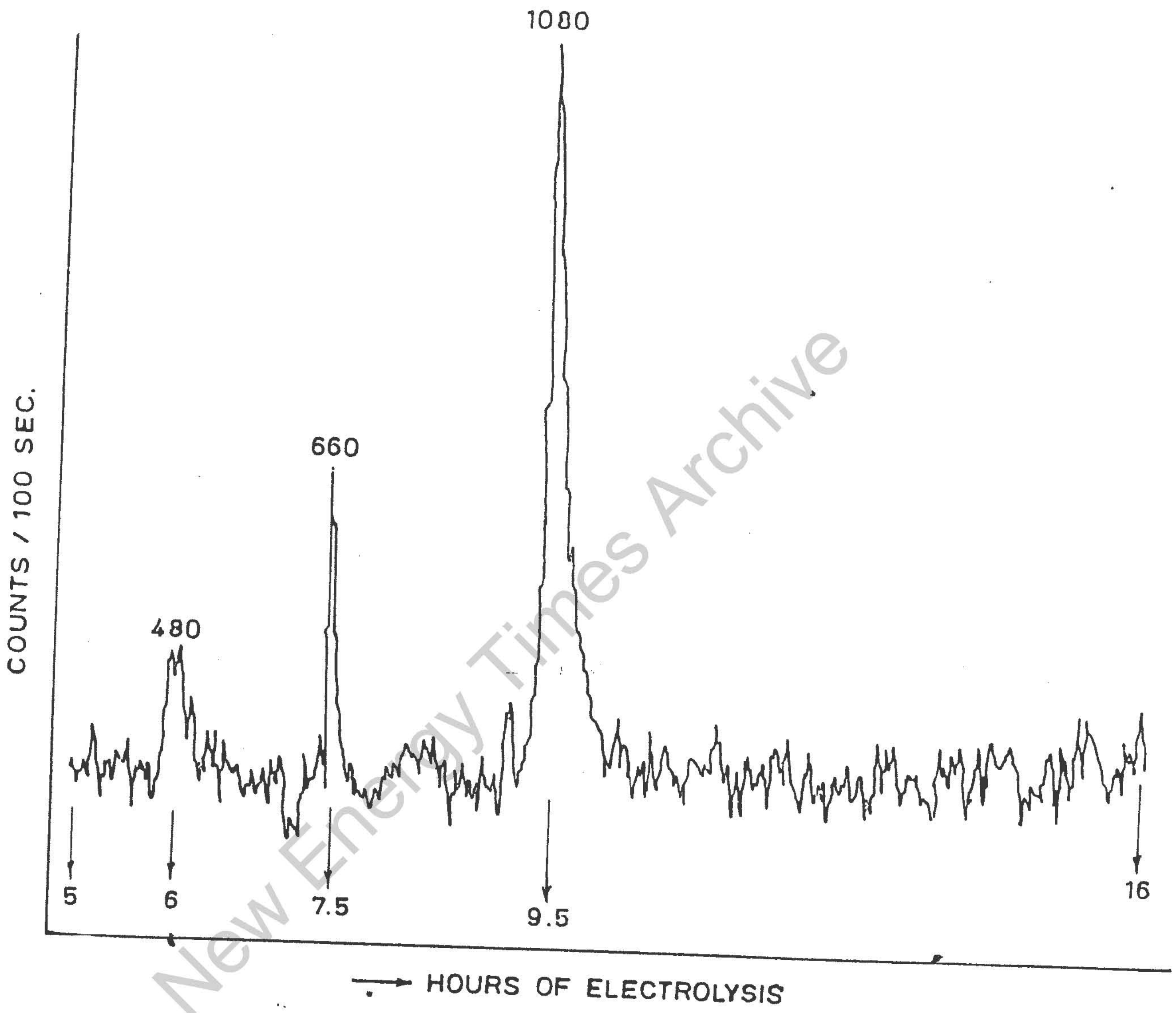
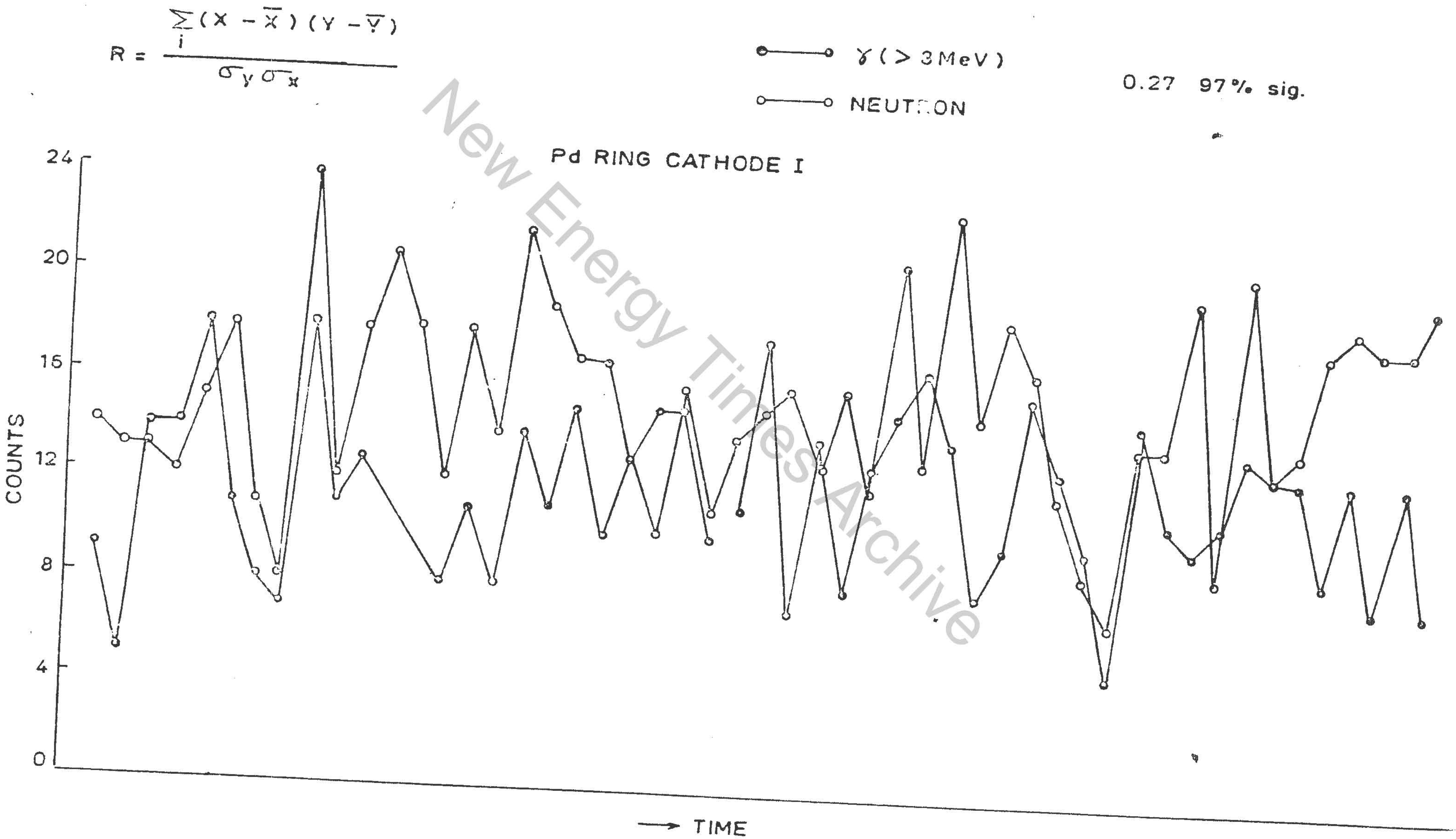


FIG. 7 COUNTS OF 1186 keV CAPTURE γ-RAY OF GADOLINIUM NaI(Tl) DETECTOR



DWELL TIME 2 min.

FIG. 8 TIME CORRELATION OF NEUTRON AND GAMMA RAY ACTIVITIES

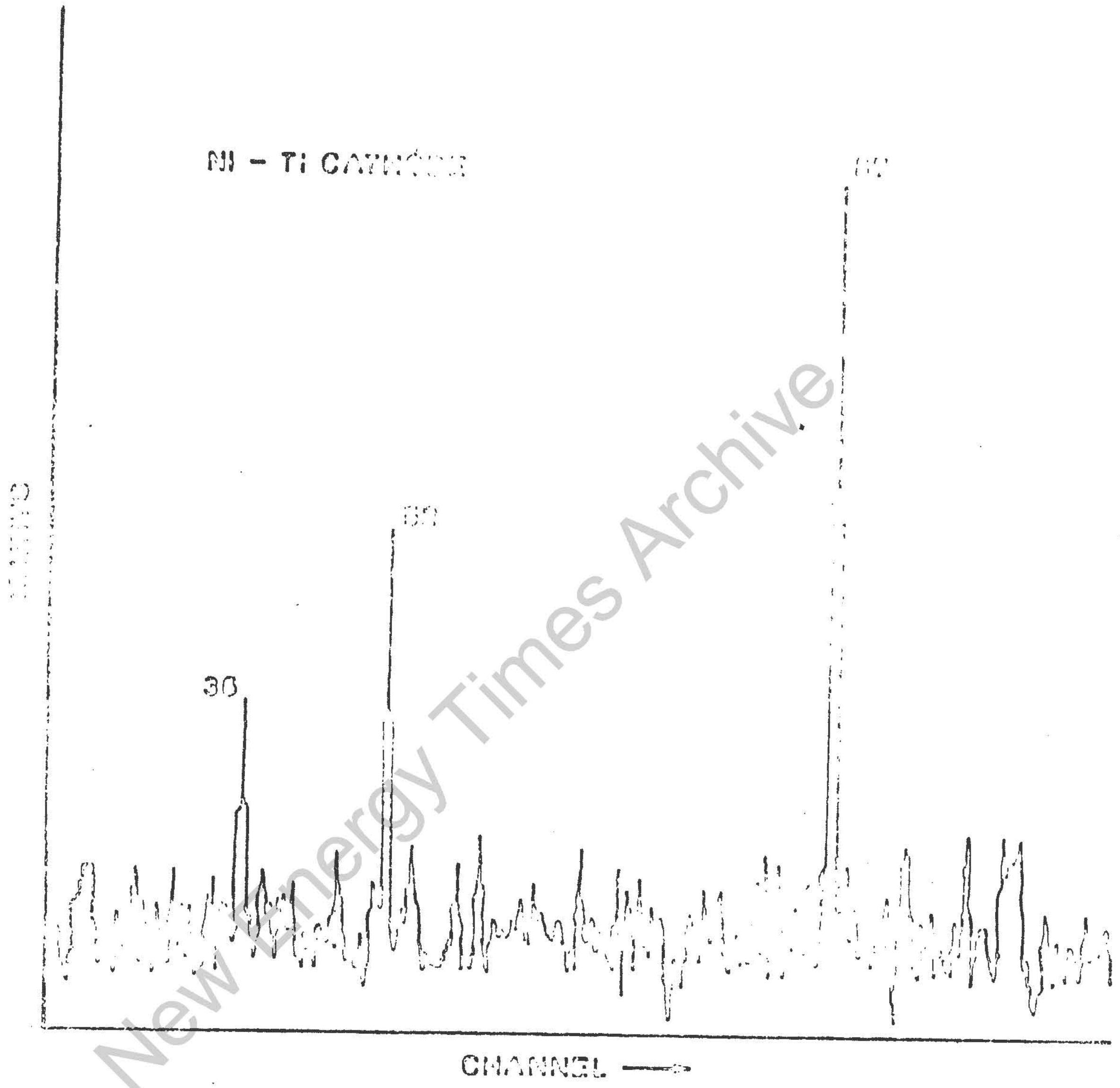


FIG. 9 DISTRIBUTION OF NEUTRON COUNTS (MCS MODE 50 SEC. DWELL TIME, Li SCINTILLATION DETECTOR)

BURST NEUTRON EMISSION AND TRITIUM GENERATION FROM PALLADIUM. CATHODE ELECTROLYTICALLY LOADED WITH DEUTERIUM

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Introduction:

Recently there have been many reports on the observation of neutrons, tritium and excess heat output from palladium and titanium cathodes electrolytically charged with deuterium[1-4]. Steady neutron count rate observed during the operation of the electrolytic cells containing these cathodes and platinum anodes were in some cases only 1.5 to 3 times the back– ground rate[3],[4] whereas in some other cases a much higher steady emission rate ($10^4 s^{-1}$) was observed. In some experiments conducted at BARC earlier neutron bursts of two orders of magnitude larger than the background have been reported from electrolytic cells[5]. The possible nuclear reaction responsible for the emission of neutrons has been inferred to be the 'cold fusion' of D atoms (existing as D+) in the metallic lattice of the cathode

$$_1D^2 + {}_1D^2 \longrightarrow [{}_2He^4]^* \longrightarrow {}_2He^3 + {}_0n^1 \qquad (1)$$

We report here a large (larger than hitherto reported) burst emission of neutrons (signal/background ratio as high as 2000) from a thin ring shaped Pd cathode during the electrolysis of heavy water at relatively low cell currents and also tritium generation as measured in the electrolyte as well as in the water reformed from the sorbed gas recovered from the cathode.

Experimental:

The electrolytic cell design was optimized mainly with respect to observation of fusion products rather than the accurate measurement of excess heat output. This is because the quantity of heat required to raise the temperature of 1 g ofD_2O even by 1 K demands the occurrence of about 10^{13} fusions (see Discussion sec.) and hence heat measurement appears to be an in–sensitive method of confirming whether cold fusion occurs in the cathode or not. Fig.1 shows the schematic of the experimental set up. The electrolytic vessel (vol. ~250 cm^3) used was made from quartz with a gas tight nylon cap. The cap had a number of penetrations for inserting electrode lead wires, thermocouple, reference electrode, purge gas inlet and outlet tubes. These tubes were made of 'Corning' glass. The Pd Cathode used was in the form of a hollow ring 2.5 cm in diameter, 1 cm in height and about 0.1 cm in thickness. The bulk density of the cathode was determined to be 12 g cm^{-3}. The cell configuration was such that the ring cathode could be charged with deuterium from both sides as it was surrounded from inside and outside by Pt gauze anodes. The anodes were loosely sandwiched between pairs of Nafion membrane so as not to allow oxygen evolved at the anode to diffuse to the cathode surface. The electrolyte was D_2O of 99.86%2 of isotopic purity containing 0.1 mol dm^{-3} LiOD and was kept under constant circulation at a flow rate of 10 $cm^3 m^{-1}$ using a peristaltic pump. Incorporation of a heat exchanger in the circulation path along with a thermostated water bath (273–373 K) served to maintain the temperature of the electrolyte (and hence the electrode) at any desired value in this range. Nitrogen gas bubbling through the cell was done to reduce the dissolved oxygen level in the electrolyte. A saturated calomel electrode along with a luggin probe containing 0.1 mol dm^{-3} LiOD/D_2O dipped in the electrolyte was used as a reference electrode to monitor the single electrode potential of the cathode.

A well type neutron detector assembly containing 24 numbers of ^{3}He detectors embedded in paraffin filled to sufficient thickness and held between aluminum cylinders for thermalisation of the neutrons was used for n detection (Fig.2a). This configuration gave 8.6% efficiency for n detection. The signals were fed in parallel to a scaler with pre–set time and to a personal computer operated in a,8K multichannel scaling (MCS)mode with dwell time of 40 seconds per channel (Fig.2b). The latter was specifically aimed at detecting any Small burst release of neutrons which can otherwise get averaged out in a longer time duration pre–set time counting.Any pickup of extraneous signals like those emanating from the operation of pump motors, drilling machines, tesla coils and fluorescent lamps going off and on was thoroughly checked and the counter was found to have good stability and was immune to such electrical disturbances. A constant background of about 1.7 counts / s was registered without the electrolytic cell in operation for a duration of 10 days before setting up the electrolytic cell inside the counter well and also during times when the electrolysis was continuing but no burst emission of neutrons occurred from the cell.

Accumulation of tritium in the electrolyte was monitored by withdrawing periodically 1 cm3 samples from the cell at about 6 days intervals and measuring the T content using gel liquid scintillation "cocktail" and a Packard counting system. The counting efficiency was about 25%. The chemiluminescence effect due to .the presence of LiOD was seen in the samples and counting was done tilll such effects died down completely and stable counting rates were obtained. The electrolytic gases from the cell were recombined over a Pt/polyester fabric catalyst and collected in a cold trap, and the resulting D_2O was checked for the presence of tritium. Loss of D_2O due to electrolysis and evaporation was made up by periodic addition of pure D_2O while losses due to samples drawn from the cell for tritium analysis were made up by adding 0.1 mol dm^{-3} LiOD solution in D_2O. The D_2O used for the experiment and for replenishments was from a single stock of heavy water. Temperature of the electrolyte was monitored by a chromel–alumel thermocouple encased in a glass tube dipping in the solution.

After the completion of the electrolysis run the Pd cathode was disassembled from the cell and connecting leads and dried. The absorbed gases from the cathode were recovered by heating it at 680 K in an evacuated chamber. From the pressure volume relationship and gas Chromatographic analysis of the deuterium content the volume of absorbed D_2 gas was computed to be 320 cm^3 at STP. This gas was then equilibrated over CuO at 680 K till there was no further reduction in volume and the water formed <–0.3 cm^3) was collected in a thimble cooled to liquid N_2 temperature and this water also was counted for T.

Results:

Figs.3 and 4 show the burst neutron emission seen from the cell. While Fig.3 shows counts obtained in the MCS mode with time, Fig.4 shows the Count rate variation with time computed from the preset time <6000 sec.) scaler counts. Upto 14 days of electrolysis (charge passed ˜2.24x10^6 Coulombs) only background neutron counts were observed and again after the 17th day of electrolysis (charge passed ˜2.5x10^6 Coulombs) till the end of the run i.e., 32nd day (total charge passed ˜3.65x106 Coulombs) only background counts were seen. During the burst Period <15th–17th day of electrolysis), initially a number of intense bursts were observed, each separated from the other approximately by.˜2 hrs of quiescent period (Fig.3). Table 1 shows the actual duration of burst and the duration of the following quiescent periods. After about 7 such bursts the burst intensity decreased but bursts became more frequent so much so that in the later stages they appeared to be continuous.

The maximum burst signal to background ratio was ~2000 (Fig.4). In terms of absolute cOunts this corresponds to counts as high as 142000 in the 40 s time channel as against 5D–70 counts registered for the background (Fig.3). The area under the curve 11.1 Fig.4 gave an integrated neutron counts of 10^7 Using the 8.6% efficiency of the counter this works out to $1.2x10^{10}$ neutrons emitted from the cell in a period of about 72 h or a pseudo average 1,neutron emission rate of $4.6x10^2$ n s^{-1} (background average rate is1.7 n s^{-1}).

The electrolyte temperature was varied in the initial stages of the run by changing the applied voltage to the cell or by changing the set temperature of the thermostatic water bath. Ten hours before the burst emission and during the burst emission, temperature of the electrolyte was not altered and it remained in between 296 K and 300 K. Electrolyte temperature at any time of electrolysis remained above 293 K.

Tritium counting of samples (Table–2) drawn from the 5th–17 th days after the burst neutron emission (sample Nos. 4,5and 6 in Table 2) showed an increase from 0.4 to 1.3 Bq.cm^3 Low level counting methods (60 minute count duration) coupled with a stable system background yielded a standard deviation of only 3% on the count rates. The cell electrolyte volume being 250 cm^3 an increase of 0.4 to 1.3 Bq. cm^{3}in tritium activity shows an extra input of T to the extent of 100 to 325Bq., amounting to 5.6–18.0 x 10^{10} extra tritium atoms accumulating in the electrolyte probably as D_2O. It is known that at temperatures above 293 K,electrolysis of D_2O does not result in preferential enrichment of tritium in the electrolyte[5] . In the present experiment electrolytic gases recombined over a catalyst and counted for tritium have shown tritium escaping from the cell. Hence the observed excess of tritium activity points to an extra source of tritium on the conservative side, i.e., not accounting for the tritium that is carried away in the gas stream during the electrolysis.

Degassing of the Pd cathode at 680 K at the end of the experiment yielded 320 cm^3 of D_2 gas at STP. By reaction of this gas over CuO turnings at 680 K and quantitatively collecting the reformed water and,counting for tritium has shown 5.4 Bq. ($3x10^9$ atoms of T) accumulating in the Pd cathode.

Fig.4 also indicates the electrode potential as observed against a saturated calomel electrode. A rest potential of –1.0 V indicates that the electrode at 0.1 mol dm –3 alkali concentration behaves as a near hydrogen electrode. Monitoring potentials some hours into the burst emission period revealed fluctuations in the working electrode potentials. A shift to more positive value (by as much as 0.7 Volts in the cell under "OFF" and by 3 Volts in the "ON" conditions) was observed when burst emission occurred. Thus it looks as if there is depletion of deuterium gas at the surface of the electrode when burst emission of neutrons takes place.

Discussion:

Since the fusion of two deuterium atoms under the ambient temperature conditions is assumed to be induced by quantum mechanical tunneling, its probability depends on the nearest neighbor distance between the D atoms. The equilibrium distance between D atoms in D_2 gas being 0.74 A. recent experimental results(1-5) showed that in order to explain the observed rates of reaction the equilibrium distance between D atoms must be greatly reduced.Sun and Tomorak[6] point out that at very high deuterium concentrations in the bulk, corresponding to a hypothetical PdD_2 crystal. the equilibrium distance between the two D atoms is increased by 0.2 A from the gas phase value of0.74 A. They conclude that because of such large internuclear distance cold fusion of deuterium is very improbable inside a palladium matrix. But the question that remains unanswered is whether D+..ion in view of its high mobility in Pd matrix can encounter a significant number of close collisions and in that process result in fusion reactions giving rise to neutron and tritium as fusion products from reactions such as

$$_1D^2 + {}_1D^2 \longrightarrow {}_2HE^3(0.8.2MeV) + {}_0n^1(2.45MeV) \quad (1)$$
$$_1D^2 + {}_1D^2 \longrightarrow {}_1T^3(1.01MeV) + {}_1H^1\,(3.02MeV) \quad (2)$$

The present study has shown that for identifying whether cold fusion occurs or not, monitoring neutrons is a much more sensitive method than monitoring tritium, especially when the fusion events generating tritium are not very high .This is because of the Small value of the decay constant of tritium which requires an accumulation of 10^9 atoms to register 1 Bq. of tritium activity. In the present case although the neutron emitting events computed from the integrated neutron counts amounted to only 10^8 as compared to 1011 events computed from tritium data, the neutron emission occurred with big spikes and bursts. As against this, 10^{11} events through the tritium channel were inferred from an increase of 1.3 B9./cm^3 extra tritium activity observed at the end of the experiment. Since the volume of the electrolyte used was 250 cm^3 the above tritium concentration amounts to about 325 Bq.of tritium activity (1.8 x 10^{11} T atoms) held in the electrolyte. In contrast with the total number of T atoms released to the electrolyte, it was found that only 5.4 Bq of tritium activity (3 x 10^9 T atoms) were held in the pd cathode. But even this 5.4 Bq of T held in the cathode is 7 times more than what one would have obtained even if one takes into account back diffusion of tritium from the electrolyte to the Pd electrode. Since electrolysis of D_2O at> 293 K does not result in T enrichment in the electrolyte, this back diffusion can only result in the the same T activity concentration in the reformed water,obtained by degassing the absorbed gases in the cathode and recombining over a catalyst, as is present in the original D_2O taken in the cell. The diffusion of T from electrolyte to Pd cathode would have given rise to a maximum of 0.72 Bq of T activity built up in the cathode over the duration of this experiment. But the actually observed activity of 5,4 Bq Shows that extra T has got generated in the Pd cathode. But it 100k5 as if the generated T most)y diffuses into the electrolyte rather than getting retained in the Pd matrix which is somewhat akin to n emission. $rom the variation in T activity observed at different times during the course of electrolysis (Table–2) it appears that T input into the electrolyte started after the hurst n emission occurred since the 16th day sample which was taken during the burst n emission registered the same T activity as the sample taken id the initial stages of the run.. But during the T generation period (17th–32nd day) there was no n emission observed over the background rate.

From the volume of D_2 gas trapped inside the Pd electrode8 (320 cm^3 at STP actually collected) the composition of Palladium–Deuteride that would have given rise to the burst n emission was inferred to be between $PdD_{0\cdot3\text{-}0\cdot4}$ Using the known diffusion coefficient of D <lxlO^{-7} cm^2/s) lt was computed that through the 1mm thick cathode used in this study, D atoms can enter and come out through the other side in about 30 hours time thus pointing to the attainment of at least $PdD_{0\cdot25}$ configuration in about a day's time. But, as shown by D_2 gas trapped in the cathode at the end of the experiment (32 days), only at the end of the 32nd days this composition seems to have been reached. The reason for this could be the blackish loose coating forming on the Pd Cathode during the course Of the experiment which perhaps acted as a diffusion barrier for the entry of D atoms. EDXF analysis of this coating revealed it to be platinum which might have arisen from anodic dissolution of pt at the applied cell voltages. (Which were higher than the reversible pt/pt2+ potential). The reasons for not sustaining the burst neutron emission for more than three days could be summarized as follows: Those sites in Pd matrix in which fusion of D atoms occurred might have been the really active site@ and once D atoms got depleted from those sites further replenishment did not take place possibly either because of the barrier coating which only favoured molecular D_2 formation

from the cathode surface with no further entry of D atoms into the matrix or because such sites had turned amorphous due to the intense local heating that might have occurred from the deposited kinetic energy of the fusion products.

The literature reports on cold fusion describing the large heat output from Pd electrodes of different configurations is rather confusing. In general very few groups have been able to reproduce the large heat output reported by Fleischmann et al[1] and Mathews et a1(4) Il@ our laboratory we have carried Out several runs on electrolytic cells using Pd cathodes of various shapes and dimensions (including a solid cylinder 1 cm diameter and 1 cm long) and pt anodes in 0.1 mol dm^{-3} $LiOD/D_2O$ along with control runs using both electrodes of Pt in the same electrolyte as well as Pd cathodes and Pt anodes in 0.1 mol dm^{-3} LiOH/H2O and were not able to observe any excess heat output within the .limits 0$ uncertainty of our calorimetry, Which is estimated to be about ± 10%. In fact, by comparison with experiments where the cell contents were heated by a kanthal wire heater, we found that in "both control and actual experiments, the observed heat output from the electrolytic cell (under steady Conditions) was the same as the electrical power input (VXI),making one wonder, as done by Santhanam et a1(3) as to where from the power required to sustain the electrolysis comes. The answer must obviously be that such comparisons, even after taking precautions to stir the system are subjected to various sources of error, and in our view very precise and unambiguous electrolytic calorimetric experiments which can detect heat output corresponding to steady excess temperature of 0.1 – 1 K are yet to be reported. Even to match a cooling rate of 0.1 K per minute in a cell of dimensions reported in the present paper it would require the occurrence of fusions at a steady rate of about 10^{10}/s. As discussed above. the observations of n bursts revealed that the occurrence of fusions is not at a steady rate of the desired magnitude and hence there is no wonder that the excess heat output went undetected.

No significant heat generation was observed in the present study and heat generated in cold fusion if any, could not be differentiated from the background Joule heating. Considering the total number of fusion events that occurred and the heat capacity of the system it is not surprising that no significant temperature rise was observed.

Conclusions:

The present study has shown evidence for cold fusion phenomenon in an electrolytically charged Pd matrix in terms of neutron and tritium as the signatures. The tritium channel seems to be favoured over the neutron channel.During the period of our experiment a total of 10^{11} fusion events leading to tritium generation were observed whereas the neutron channel accounted for Only 10^{8} fusion events.No significant heat output over the Joule heating could be observed.The present study has also revealed that the effect is small and not a sustained one. Energy production from cold fusion of deuterium in an electrolytically charged Pd matrix in a sustained manner may require more systematic exploration to identify the various parameters governing the occurrence of the process,not the least important among which is the proper pretreatment of the electrode.

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Table-1

Duration of burst neutron emission and that of the intervening quiescent periods from the Pd-Pt electrolytic cell

Burst No.	Duration of each Burst (h)	Duration of intervening quiescent period (h)
1	2.6	
		0.25
2	2.1	
		2.4
3	2.0	
		3.3
4	1.0	
		2.8
5	0.2	
		1.2
6	0.3	
		1.1
7	0.05	
		0.5

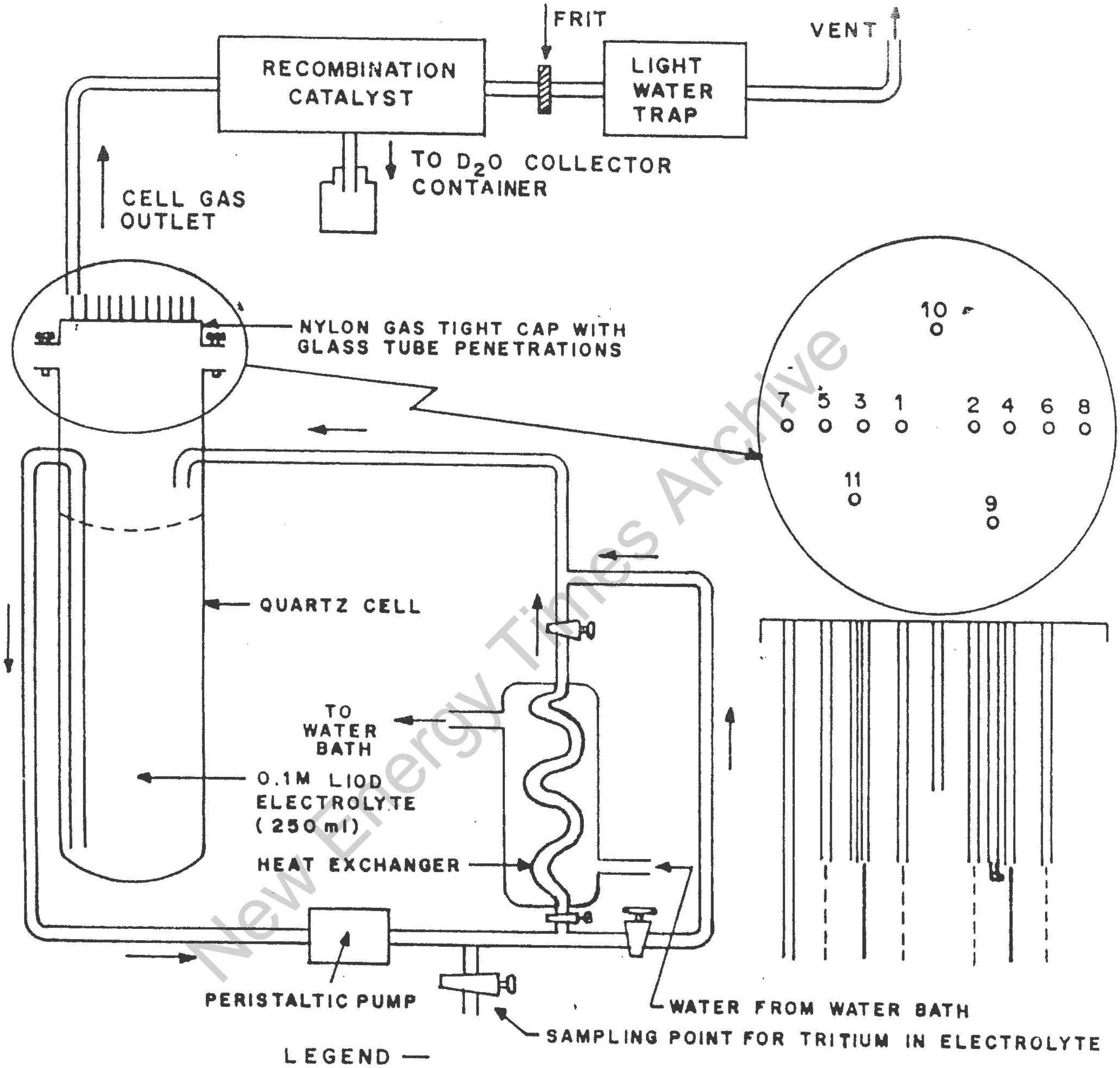
After the last quiescent period following the 7th burst almost continuous emission of neutrons at different rates was observed.

Table-2

Tritium content in the electrolyte (0.1M LiOD)
of Pd-Pt electrolysis cell

Sample No.	Duration of electrolysis (d)	Coulombs passed (cumulative) ($\times 10^{-6}$)	Tritium activity (Bq/ml) *
1	0	0	3.65
2	7	1.07	3.32
3	16	2.36	3.65
4	20	2.72	4.94
5	26	3.21	4.24
6	32	3.55	5.2

* standard deviation : ± 3 %



LEGEND —

1,2 – INNER CYLINDRICAL ANODE (Pt)
3,4 – CATHODE RING (Pd)
5,6 – OUTER CYLINDRICAL ANODE (Pt)
7 – GAS INLET
8 – GAS OUTLET
9 – LUGGIN PROBE FOR CALOMEL ELECTRODE
10 – Cr – Al THERMOCOUPLE
11 – D_2O REPLENISHMENT INLET

FIG. 1 EXPERIMENTAL ASSEMBLY – SCHEMATIC.

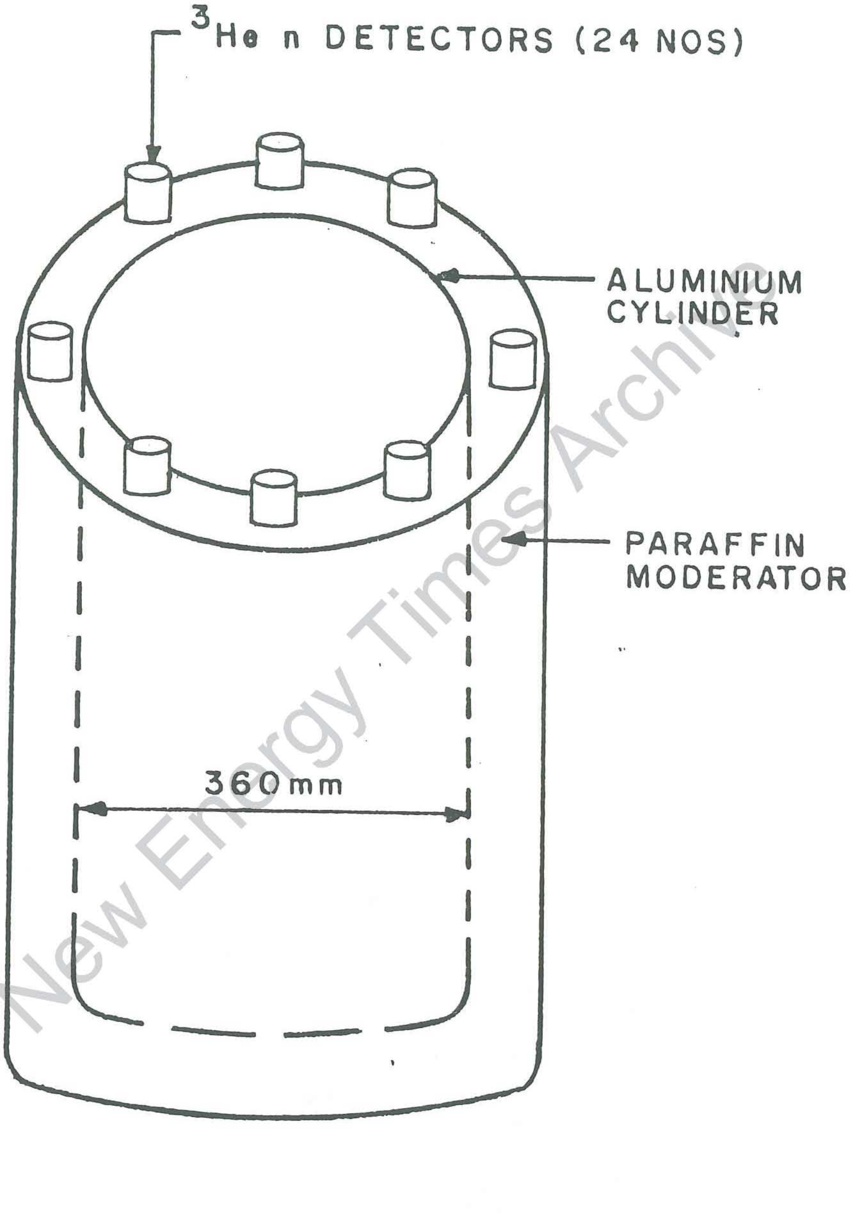


FIG. 2a WELL-TYPE n DETECTOR

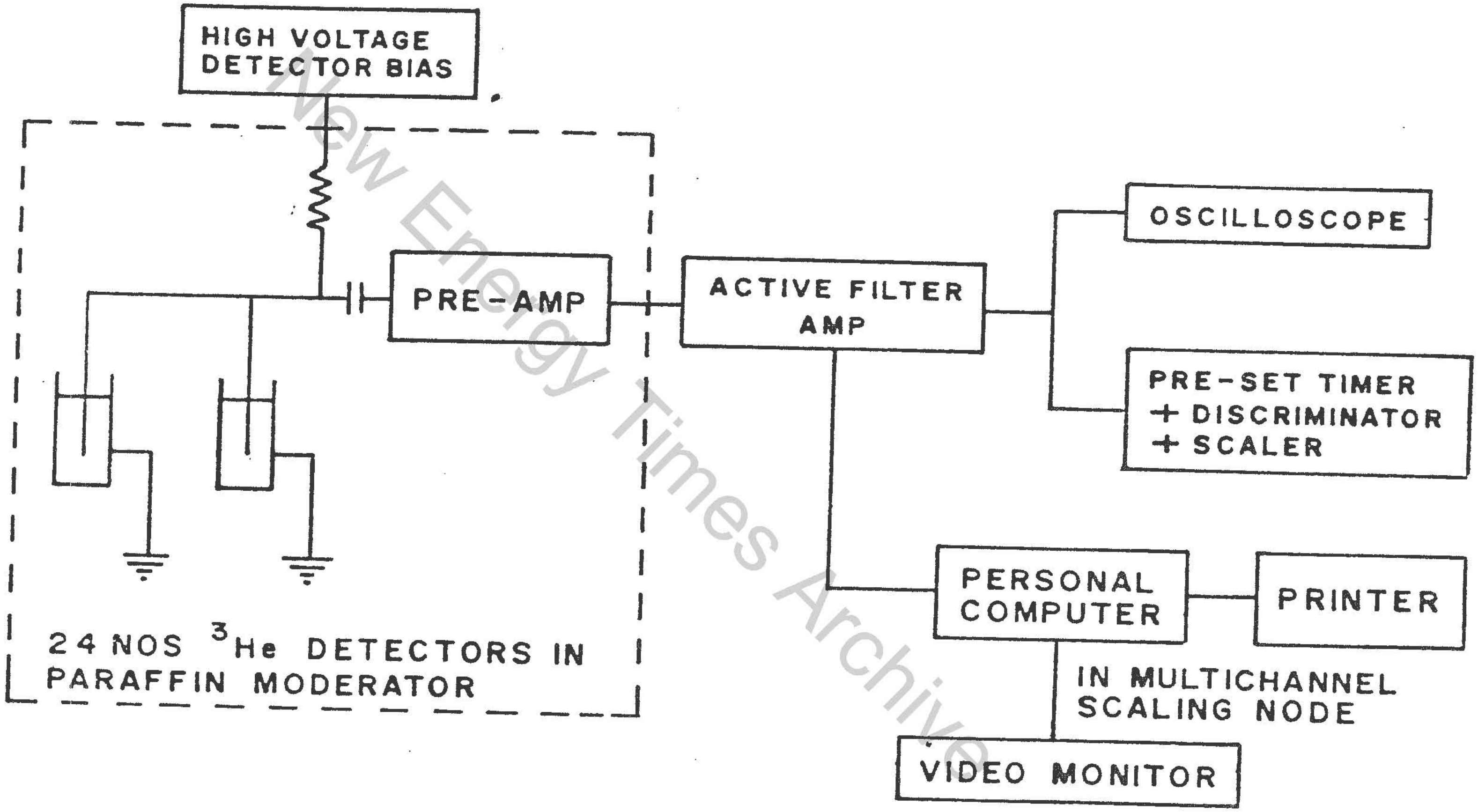

HIGH VOLTAGE DETECTOR BIAS
PRE-AMP
ACTIVE FILTER AMP
OSCILLOSCOPE
PRE-SET TIMER + DISCRIMINATOR + SCALER
PERSONAL COMPUTER
PRINTER
IN MULTICHANNEL SCALING NODE
VIDEO MONITOR
24 NOS ^{3}He DETECTORS IN PARAFFIN MODERATOR

FIG. 2b SETUP OF NEUTRON COUNTER.

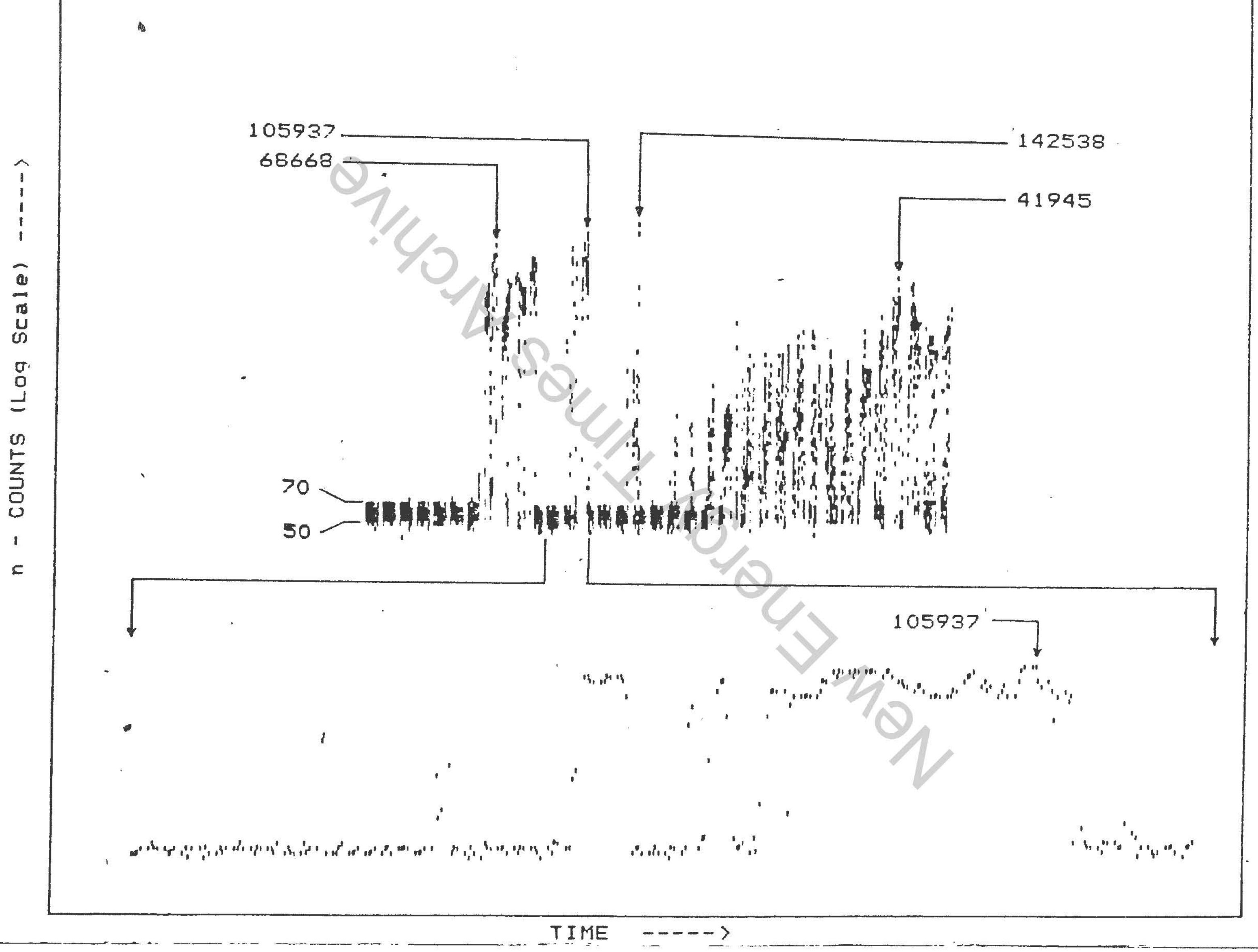


Fig.3. Burst neutron emission in MCS mode with time

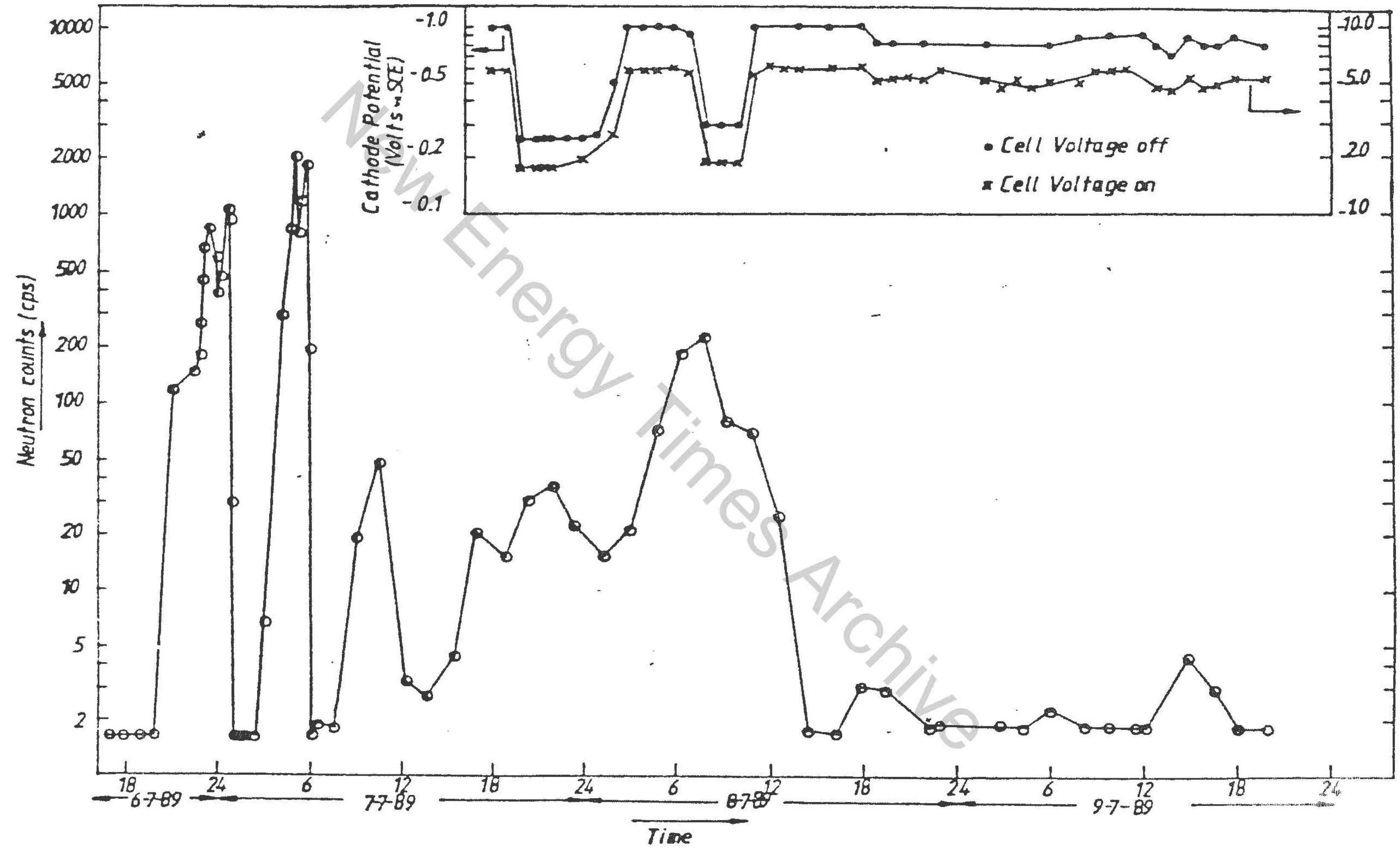


Fig.4. Burst neutron emission rate and Cathode Potential variation with time

BARC Studies in Cold Fusion

Search for Helium in the electrolysis of D_20 with Palladium Cathode

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In nuclear fusion reactions involving D_2 helium may be one of the possible products. During@ electrolytic dissociation of D_20 with Platinum/Palladium electrodes if any fusion reaction ([1],[2]) is taking place via the helium pathway with helium escaping to the gas phase it should be possible to detect and estimate the yield quantitatively. Helium is reported to have been observed in excess of the background in the electrolysis experiments conducted at the University of Utah([1]) The number reported is of the order of 10^{12} atoms per second (– 0.013 ul per hour). In presence of large excess of D_2 and 0_2 generated during electrolysis detection of He^3/He^4 in the gas phase poses many problems. Among the methods available for the detection of low amounts of helium gas chromatography (GC) and mass spectrometry (MS) are normally preferred. However in this case mass spectrometry (MS) is complicated since helium is in trace concentration and large excess of D_2 will interfere with the signal due to He^3 or He^4 ions unless fractional mass difference method is adopted. In order to concentrate the helium in the gas phase an experimental technique has been devised wherein D_2 and 0_2 generated by electrolysis is catalytically recombined in situ facilitating gas collection over long periods of electrolysis. The results obtained by this technique followed by gas chromatographic analysis are given in this paper. Though GC/MS analysis of the enriched sample may be more conclusive, a suitable GC/MS gas inlet interface compatible with D_2/He is difficult to get.

Experimental:

The electrolysis cell and the gas manipulation system is shown schematically in figure 1. This consists of a glass cell carrying a ground glass joint wit)? the cap connected to a mercury manometer with a 20 ml expansion bulb at the bottom, a silicone septum carrying vacuum tight electrode leads and a vacuum stopcock connecting the cell to a modified Toeppler pump with facilities to measure the gas pressure, volume and also to pressurize and transfer the collected @ae to a syfin@e salnplil3@lnanifold through a three way stop cock([3]). The third limb of this stop cock is connected to rotary vacuum pump. The catalyst for recombination of D_2 and O_2 at room temperature is a specially prepared platinum catalyst deposited on a thick synthetic fabric. It is freely suspended on the top inner side of the electrolysis cell. The catalyst has been independently assessed for $H_2/0_2$ recombination efficiency and found to have $T_1/_2$ for H_2 reaction of less than 15 seconds in presence of sufficient 0_2 with gas volumes upto about 500 ml. The gaseous products are analysed by gas–chromatography using thermal conductivity detector either (1) or) a 5meter x 3 mm id molecular sieve 5A Column at 250c with argon carrier gas which gave clear separation between helium and hydrogen for the analysis of trace amounts of helium in the sample or (2) on a 2meter x 4 mm id. molecular sieve 5A column–at 25 with with helium carrier gas for the analysis of H_2(Or D_2)' 02and N2 in the sample. The lowest almost of helium detectable in the presence of large excess of hydrogen under the experimental conditions is about 0.01 ul (or about 1 ml sample with 10 ppm He). The second column provided a reasonably good analysis for the composition of the residual gas with respect to major constituents. Total volume of the electrolysis cell and the gas manipulation system as well as the volume of each segment of the system has been determined;d to facilitate computation of the gas volumes and composition at any stage of the experiment. The electrolysis experiment has been carried out in three stages. In these experiments 20 ml of 0.1 M LiOH or LiOD is used as the electrolyte. Experiments I and II are carried out with stainlesssteel Cathode and Anode mounted in concentric tubular configuration with 1 mm electrode spacing. The electrodes are approximately 1.5 cm X 3 cm X 0.04 Cm in size. These experiments are used to test the system with respect to leak tightness, gas recombination efficiency, trace helium recovery and analysis. Experiments III to VI are carried out with palladium/platinum electrodes. In this case a palladium pl"ate (1 cm X 1.5 cm X 0.15 cm) is sandwiched between two platinum plates (1 cm X 1.5 cm X 0.05 cm).

Prior to starting electrolysis the entire system including the cell with 20 ml electrolyte is evacuated through the threeway stop cock to thoroughly degas the electrolyte. After attaining vacuum the cell is isolated from the pump and rest of the system and the electrolysis started and continued for the required duration by connecting the electrodes to a D.C. power supply. At the end of the electrolysis the power is put off,system is allowed to stabilize till no further change in the mercury level of the manometer is noticeable. At this stage by suitable manipulation of the three stop cocks and mercury reservoir gas transferring, compression,measurement of pressure and volume and sampling for analysis are carried out. Whenever necessary desired reactant gas is introduced into the electrolysis cell through the silicone septum carrying the electrodes by means of a syringe. The electrolysis cell isolated under vacuum is found to retain vacuum for more than 48 hours(drop in mercury level – 0.5 cm). The results of the experiments with relevant details are given in Table 1.

Conclusions:

1) In contrast to the stainless steel electrodes Palladium cathode/Palladium anode configuration resulted in D_2 deficient gas composition and Palladium Cathode/Palladium anode configuration showed O_2 deficient gas. In the initial stages of electrolysis much of the hydrogen (or D_2) may be absorbed by palladium reaching equilibrium in about 2 1/2 hours as indicated by the steady pressure build up.

2) Though all the released gas is contained and concentrated to residual 1 to 3 ml Volume no helium could be detected in all the experiments.

3) Hydrogen (or D_2) absorbed on the electrode is slowly released under vacuum Platinum catalyst can be incorporated in the cell design to recombine the evolved gas thus facilitating D_2O recovery and also possible recovery of any gas phase back into the aqueous phase.5) In case an independent proof, for the cold fusion via the helium pathway is available, this method can be adopted suitably to detect helium and substantiate the finding with the possibility of unambiguous evidence obtainable from GC/MS analysis of the concentrated residual gas.

Explanatory note to the Table:

(a) In case of I and II electrolysis is carried out for varying duration to ascertain the viability of the method and recombination efficiency of the catalyst.

(a)* In these cases 150 ul of 1 % He in argon is added to the cell prior to electrolysis and the residual gas at the end analysed for He. Recovery is found to be better than 90%. (b)

(b) (i) In case of III to VI initial evacuation of the system is carried out with the D.C. potential for about 5 minutes, then evacuation continued with the potential off for about 5 minutes, system isolated and the regular electrolysis carried out (system purging).
(ii) In these cases mercury level in the manometer showed a steady drop for the first 2 1./2 hrs and then slowed down.

(b)++ In case III the residual gas is used up in analysing for trace helium. Hence D_2:O_2

composition is not determined.

C) At the end of experiment IV the electrolysis cell is maintained in the isolated mode overnight. The mercury level dropped by about 2 cm. overnight and the residual gas on analysis showed 90% D_2 indicating release of D_2 under vacuum from the electrode.

Acknowledgement:

The author is obliged to Dr. N.M. Gupta and A.D. Belapurkar of Chemistry Division for providing the platinum catalyst. The author is also thankful to Dr. R.M. Iyer, Director, Chemical Group and Dr. J.P. Mittal Head, Chemistry Division for their keen interest and helpful suggestions during the course of this work.

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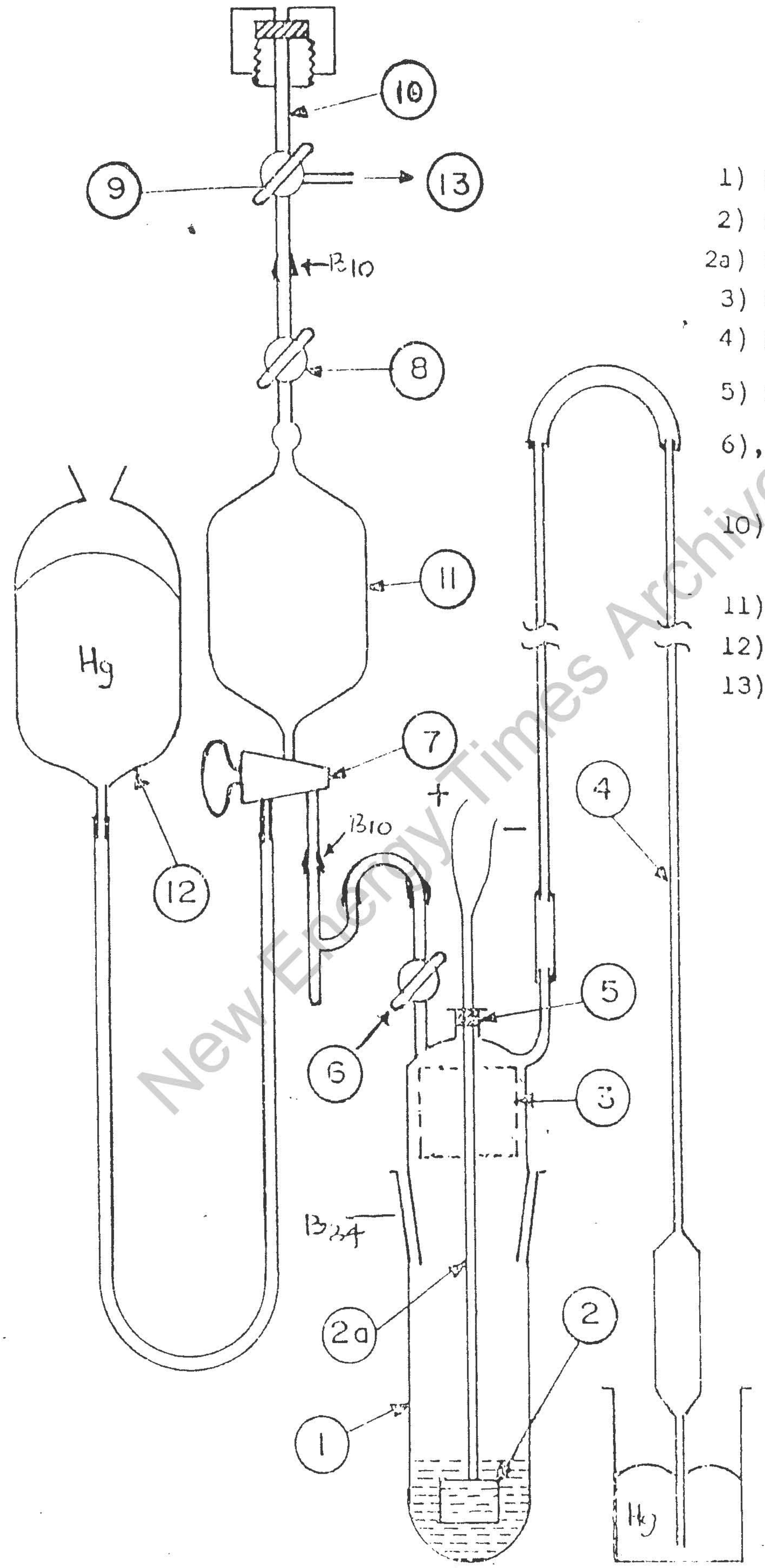
2. C.K. Mathews, G. Periaswami, K.C. Srinivas, T. Gnanasekaran, S. Rajan Babu, C. Ratnesh and a. Thiyagarajan. Indian J. of Technology 27,(1989) 229–231.

3. K.A. Rao, R.M. Iyer, Indian J. of Technology 16, (1978)44– 45.

Table 1

Experiment	$I^{(a)}$	$II^{(a)}$	$III^{(b)}$	$IV^{(b)}$	$V^{(b)}$	$VI^{(b)}$
Electrodes	Concentric Stainless Steel Cathode and Anode	Concentric Stainless Steel Cathode and Anode	Palladium Cathode Platinum Anode	Palladium Cathode Platinum Anode	Platinum Cathode Palladium Anode	Palladium Cathode Platinum Anode
Electrolyte	LiOH, 0.1M in H_2O	LiOD 0.1M in D_2O	LiOD, 0.1M in D_2O	LiOD, 0.1M in D_2O	LiOD, 0.1M in D_2O	LiOD, 0.1M in D_2O
Electrolysis Voltage Current and Duration	4.0 V ~250 mA 1h & 2h*	4.0 V ~250 mA 2h*, 2h, 4h 1h*, 6h, 6h	4.0 V ~250 mA 3h	5.0 V ~500 mA 6h	4.5 V ~450 mA 2h	4.0 V ~275 mA 6h
Residual gas Volume after Electrolysis and Composition (25^oC/ 76 cm Hg)	~1 ml $H_2:O_2$ ~2:1	~1 to 3 ml $D_2:O_2$ ~2:1	26 ml ~90% O_2	16 ml ~90% O_2	48 ml ~94% O_2	28 ml ~94% O_2
Volume of reactant gas added	---	---	50 ml H_2	30 ml H_2	24 ml O_2	46 ml H_2
Final gas volume and composition	~1 ml $H_2:O_2$ ~2:1	~1 to 3 ml $D_2:O_2$ ~2:1	~3 ml --- (++)	~1.6 ml $D_2:O_2$ ~1:5 (c)	~1.1 ml $D_2:O_2$ ~4:1	~5.6 ml $D_2:O_2$ ~1:8



1) Electrolytic cell
2) Electrodes
2a) Electrode leads
3) Catalyst fabric
4) Manometer
5) Silicone Septum
6),(7),(8) & (9) Vac Stop cocks
10) Sampling manifold with Septum
11) Expansion bulb
12) Mercury reservoir
13) To vac pump

Fig. 1 : Electrolysis cell and gas handling system.

BARC Studies in Cold Fusion

Microcalorimetric Investigations on the Differential Heat evolved in Electrolysis of H_2O and D_2O

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Microcalorimetric investigations were carried out to evaluate differential heat evolution in the electrolysis of D_2O and H_2O in presence of 0.1 M LiOD or LiOH as an electrolyte. A calvet type (Setaram,C–80) microcalorimeter was employed for this purpose. Two identical stainless steel cells (height 8 Cm, inner diameter 1.5 Cm)were equipped with similar Pd and Pt electrodes of 0.1 and 0.2 Cm .–diameter respectively the length of both the electrodes being 7 Cm. The differential heat evolution was measured for different current density values.

Prior to electrolysis experiments, the thermal balancing of the two cells was attained by adjusting the volumes of the D_2O and H_2O in the two cells. Both the cells were heated at the identical predetermined linear rate in the range of 0.2 and 2^0C min. It was observed that the best match between the two cells could be obtained by taking 11.1 ml of H_2O and 10 ml of D_2O in two cells. With these of liquids in two cells, the cell resistances were matched by adjusting the inter electrode distances. The electrolysis was then carried–out by connecting the two cells either in the series or in parallel to a stabilized power supply. The gases evolved during electrolysis were vented out through 30 Cm long stainless steel tube of 0.2 Cm inner diameter. The evolved gas flow rate was monitored periodically using a soap film flowmeter and was found to be dependent of current density. In a typical case when 101 ml H_2O and 10 ml D_2O were used in two microcalorimeter cells the flow rate of evolved gases under equilibrium condition of electrolysis (current density 176 mA/Cm^{-2} Was found to be 1.9 ml min^{-1} for H_2O cell and 1.6 ml min^{-1} for D_2O cell. When the current density was raised to 352 mA Cm^{-2} the flow. rates were 3.53 and 3.15 ml min^{-1} for H_2O and D_2O cells respectively. A small discrepancy in flow rates of evolved gases from two cells was observed even when similar amount of H_2O was taken in both the cells.

The temperature of the microcalorimeter vessel was evaluated carefully and arise of about 0.20c for current density of 176 mA Cm^{-2} and of 0.4^0C for the current density of 352 mA Cm^{-2} was observed.

The nature of the curves obtained in microcalorimetry data indicate that one of the cells gets heated more than the other during electrolysis. This difference could be attributed to several factors such as difference in rate of electrolysis, different rate of diffusion of H and D through the outlet tube and the difference in the heat capacity of H_2 and D_2 and O_2 gases evolved in electrolysis. No conclusive evidence is, however, obtained so far to suggest that a higher heat is evolved in the electrolysis of D_2O as compared to that of H_2O under identical test conditions. Experiments are being continued to evaluate the effect of different pretreatments to palladium electrode on electrolytic behavior of H_2O.and D_2O.

Cold Fusion Investigations at ROMG through Electrolysis of Heavy Water with Pd Cathode

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Part I: Initial Experiments (22nd April to 12th May 1989)

Introduction

Following a recent publication by Pons and Fleischman on Electrochemically Induced Nuclear Fusion of Deuterium /1/ experiments were initiated in our laboratory keeping the electrolysis conditions as close as possible to those of the authors. Due to non availability of a sensitive neutron counter, initial experiments were restricted to measurements of temperature changes occurring in the electrolytic cell to study the excess heating reported by the authors in the electrolysis of heavy water with palladium as the cathode. Tritium measurements in the heavy water following electrolysis were also made. Control experiments were carried out using platinum cathode in place of palladium. In this report, a brief description of the results obtained along with electrolysis data plots is given.

Experimental Details

The Cathode consisted of a palladium tube which was used earlier in gas analysis apparatus for hydrogen absorption. Prior to its use as a cathode, it was polished to remove surface film if any and it was heated to almost red hot condition to expel any occluded gases.

Details of palladium cathode are
Length 6.0 cm; O.D 0.4 cm ; Weight 4..2 g ; Volume 0.36 cm^3 ; Surface area 7.5 cm^2
Length of cathode dipping in electrolyte solution 3.0 cm Volume of dipped portion of the electrode 0.18 cm^3 ; Surface area of dipped portion of the electrode 3.75 cm^2 ; Weight of dipped portion of the electrode 2.1 g

The Platinum Cathode used in control experiments was a Platinum rod of 2 mm dia. was cleaned and dried before use. Length of platinum cathode dipping in solution was .o3 cm. The Anode comprised of a gauze shaped into cylindrical form.

Electrolyte solution: Lithium hydroxide solution (0.1 M) with heavy water (isotopic purity > 99..86% W D_2O) as solvent.; Weight of the electrolyte solution taken for electrolysis: 86 g. ; Voltage supply for electrolysis: Constant voltage supply unit with meters for voltage and current readings; Temperature of the electrolyte solution: This was read on the thermometer immersed in the solution.

Tritium analysis; Heavy water samples after electrolysis were sent elsewhere for tritium measurement.

Cell Assembly: Fig.1 shows the cell assembly and the associated set up. There was no stirrer or gas–sparing through the solution during electrolysis. It was assumed that the gases liberated during electrolysis would help in stirring the solution.

Discussion

In the preliminary experiments, voltage–current characteristics of the cell were studied with varying anode geometry with a view to get high current density on palladium cathode. It was observed that current rose sharply with a wire–gauze anode in cylindrical form, surrounding the cathode. The variation of current with applied voltage is shown in Fig.2. Suitable geometry was then chosen so that there was no possibility of electrodes contacting each other during the course of the experiments.

With a regulated voltage supply unit, voltage remained constant in each experiment (except for small adjustments to keep the current constant in Expt. No.1). In experiments with lower applied voltages (3 – 3..5 V) current also remained constant. However, in experiments with higher voltages (4 V and above), current was found to increase as the electrolysis progressed, which could be partly due to higher temperature of the electrolyte solution.. Readings for temperature, voltage and current were taken at regular intervals. To establish whether the reported excess heating (over and above that due to Joule heating) is peculiar to Pd–D_2O system only, experiments were carried out in almost identical conditions for Pt–D_2O system where Pt and Pd are cathodes respectively, anode (Pt wire gauze) remaining the same in all the experiments.

The experimental details and some of the observed and calculated data are summarised in Table 1. Graphs have been plotted for all the experiments listed in Table 1 showing temperature changes against the input energy in W–minutes, obtained by cell current multiplied by (cell voltage – 1.54 V) and time in minutes. They are shown in Figs.3,4,5 and 6.

To calculate excess heating if any, in Pd–D_2O systems (Expts. No.1 and 3), accurate calorimetric measurements would be necessary, taking into consideration the heat lost to the surroundings. Our set up was not designed for such measurements. However, it was thought that comparison of the results obtained between Pd–D_2O and Pt–D_2O systems would help in establishing the excess heating observed by Pons and Fleishmann in their paper mentioned earlier. Experiments No. 2 and 4 were carried out ;for this purpose.

Thus comparing the results in Expt.1 with those in Expt. No. 2 for Pd–D_2O and Pt–D_2O systems respectively on the basis of similar rate of Joule–heating and other factors such as heavy water equivalent of the cell and its contents remaining almost identical, the T (i.e. the difference between the temperature at any given interval of time and initial temperature of the cell) observed in both the cases at any given W. minutes did not differ by more than a degree centigrade. This can be seen in Figs 3 and 4. The same data are superimposed in Fig.7 for better comparison. Under similar conditions, (Pd rod 0.2 x 10 cm; current density 64 mA/cm2) the excess rate of heating calculated from Table 1 in the paper of Pons and Fleischmann would give a value of 0.28 W for the Pd cathode in our experiment. This should give more than 60% additional heating in Pd–D_2O system as compared to that in Pt–D_2O system. This was not observed as can be seen in Fig.7.

Similar experiments (Expt. No. 3 and 4) were carried out at higher applied voltages and hence at higher current densities. According to the results of Pons and Fleishmann in Table 1 of their paper (Pd rod 0.2 x 10 cm), the excess rate of heating increased with current density. By taking the factors from their Table for the expected excess rate of heating, the calculated values for Expt. No.3 are 0.42 – 0.63 W which correspond to about 23 per cent additional heating in Pd–D_2O system as compared to that in Pt–D_2O system. Fig.5 and Fig.6 show the temperature profiles for Pd–D_2O and Pt–D_2O systems respectively and Fig.8 shows the superimposed plots. Here also, there is no indication of any excess heating in Pd–D_2O system.

Table 1

Summarised data of Electrolysis Experiments

Anode: Platinum wire gauze as given in 2.2

Expt. No.	Cathode	D_2O	Volts (V)	Current (A)	Current Density mA/cm^2	Duration of Expt. 't' (min)	Final temp. (°C)	ΔT (°C)	(V-1.54) (V)	Watts range (W)	Σ W-Min at 't' min
1.	Pd-tube	D_2O	3.15 - 3.35	0.25	67	285	37.9	9.2	1.61 - 1.81	0.40 - 0.45	124
2	Pt-rod	D_2O	3.5	0.22 - 0.23	60	285	37.0	8.4	1.96	0.43 - 0.45	124
3.	Pd-tube	D_2O	5	0.5 - 0.8	134 - 213	100	50.3	22.1	3.46	1.73 - 2.77	208
4.	Pt-rod	D_2O	5.5	0.45 - 0.60	~300	91	49.8	21.6	3.96	1.78 - 2.38	210

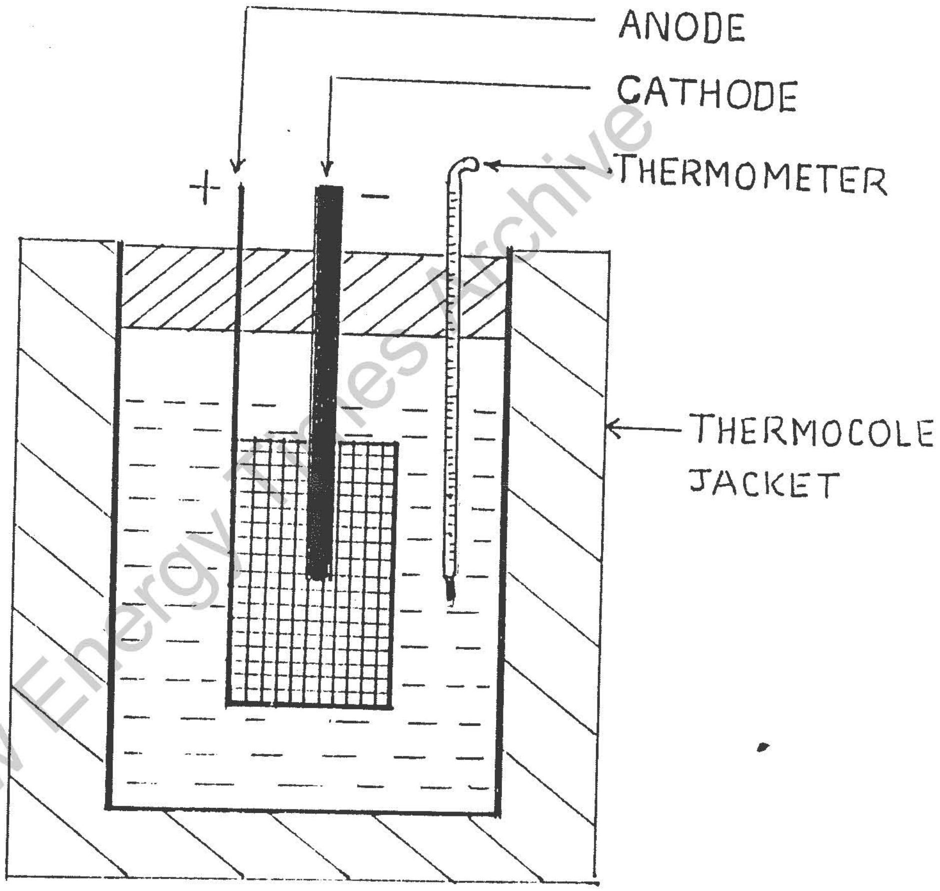


FIG. 1 CELL FOR ELECTROLYSIS

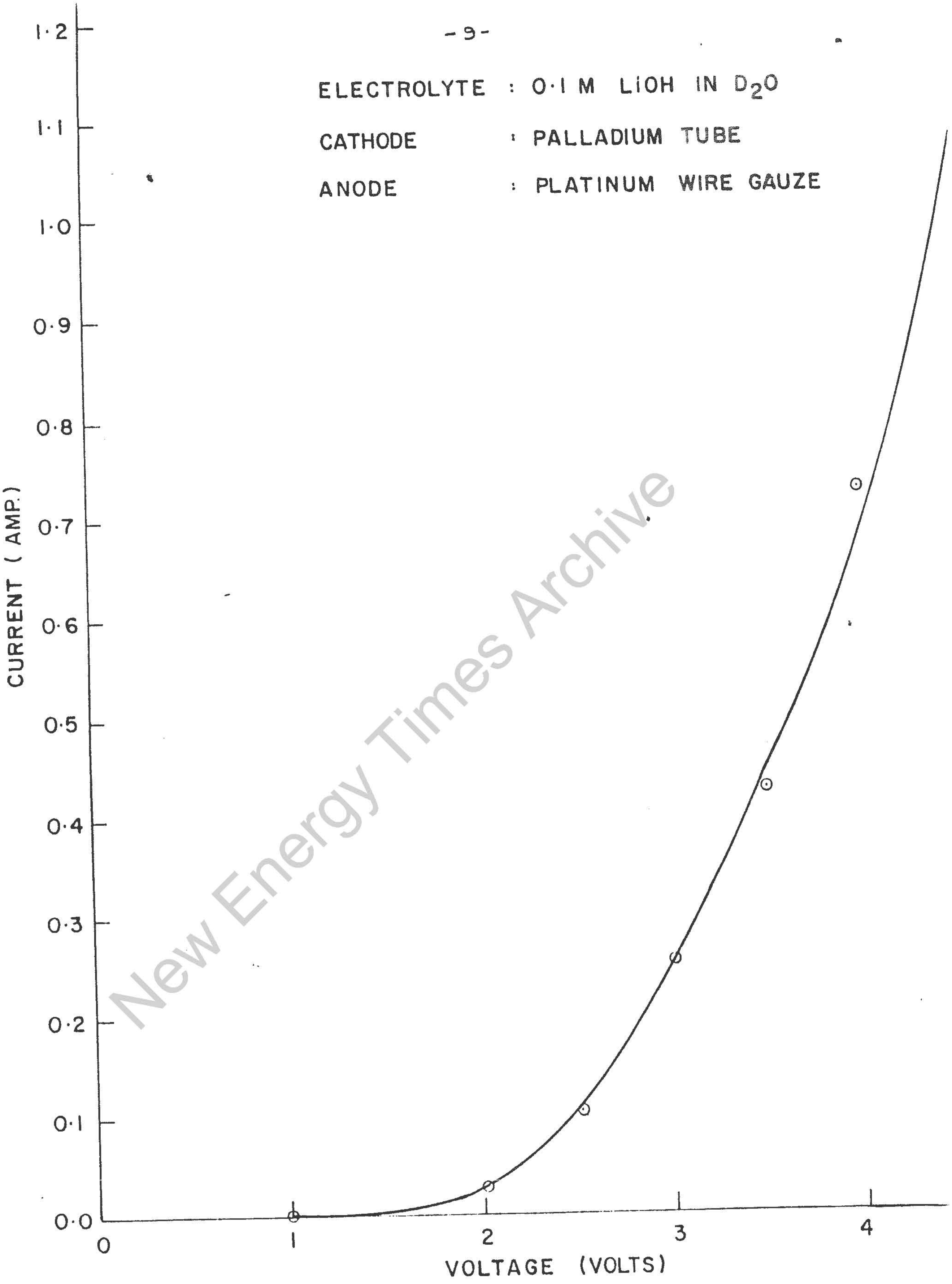


FIG. 2 CURRENT Vs. APPLIED VOLTAGE

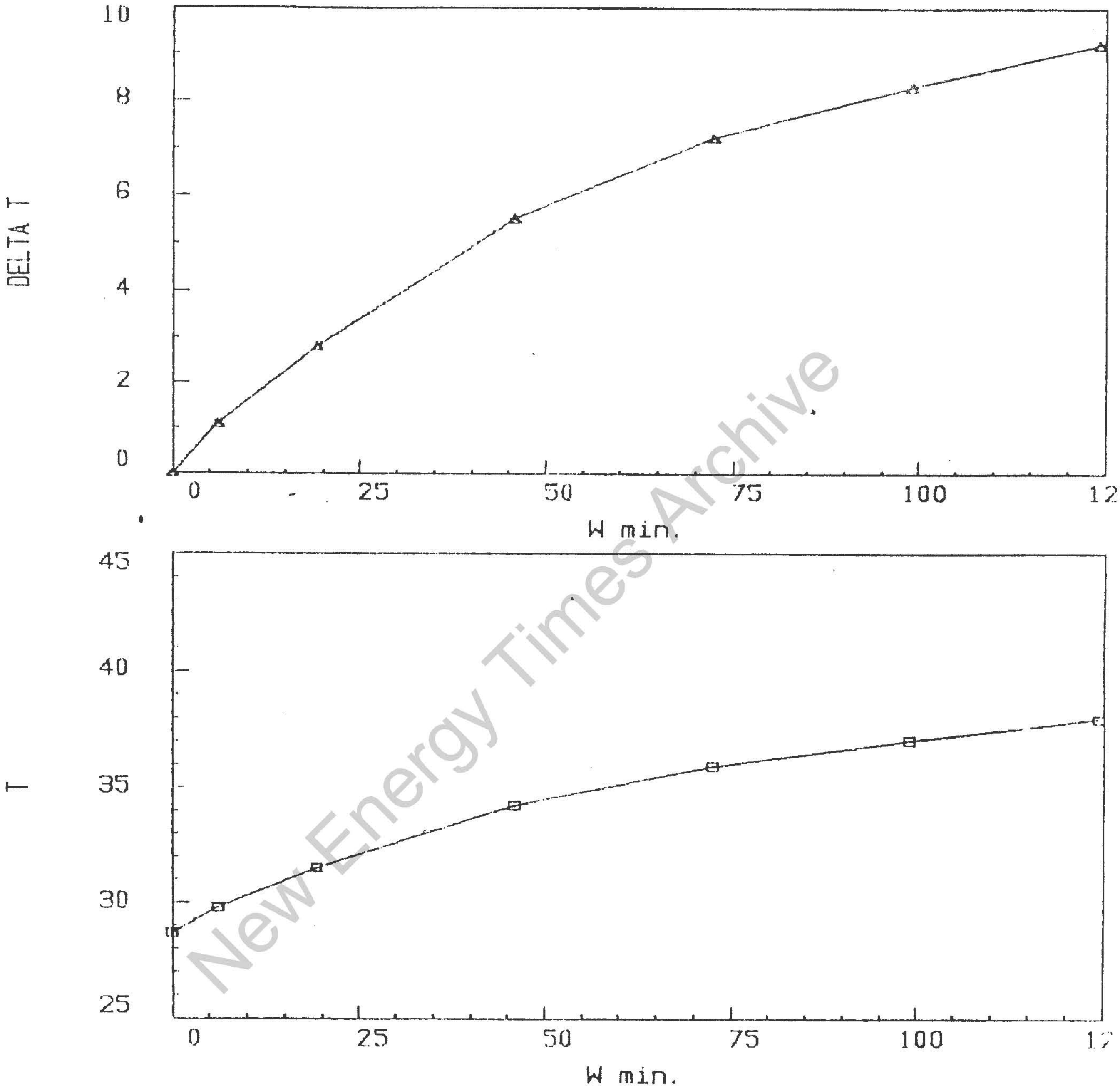


Fig 3. Expt No.1 PD-CATHODE, Pt-ANODE, D2O SYSTEM
VOLTS 3.15-3.35, CURRENT 0.25 A

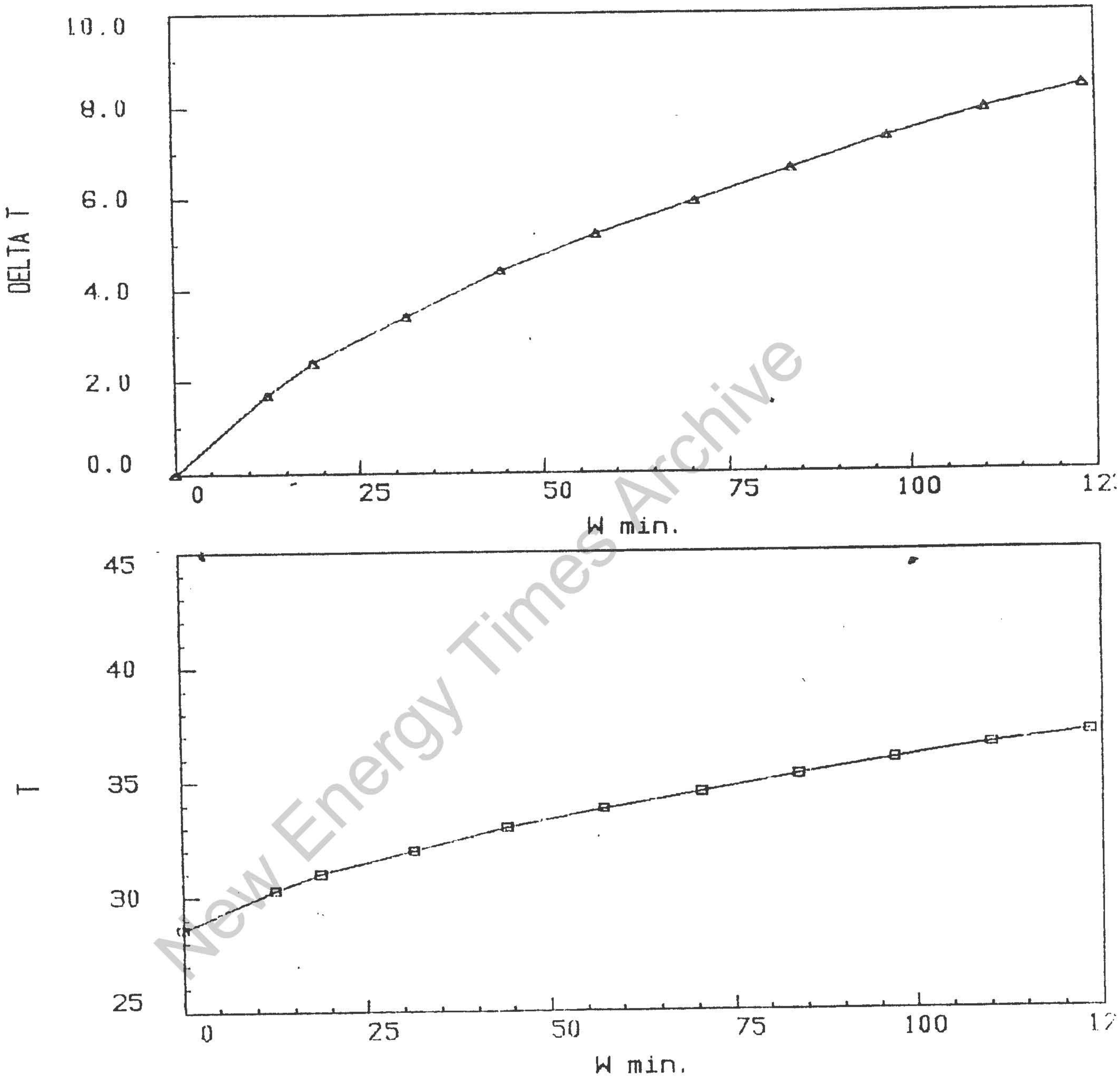


Fig. 4 PT-CATHODE, Pt-ANODE, D20 SYSTEM
VOLTS. 3.5, CURRENT 0.22-0.23 A

Expt. No 2

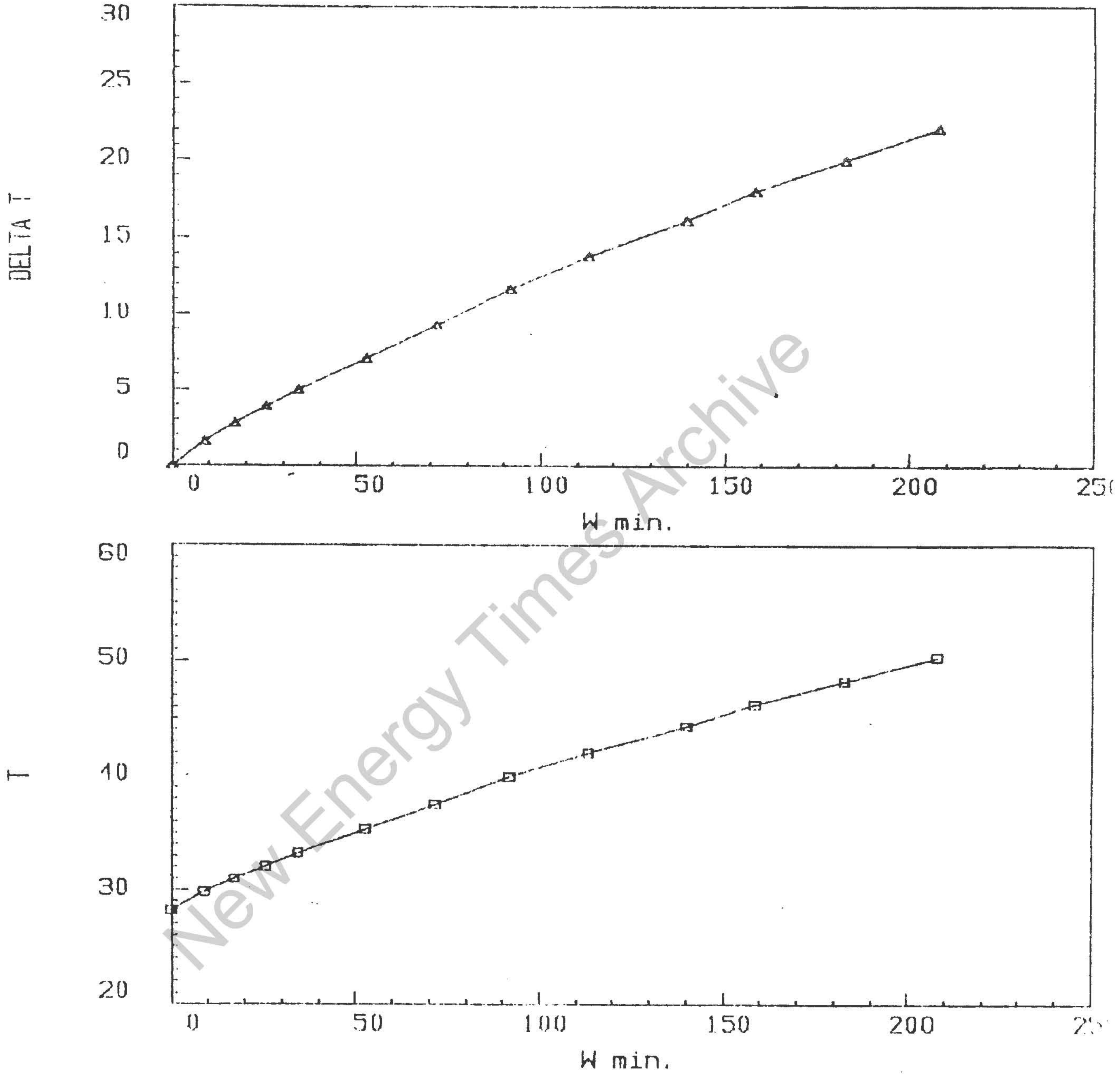


Fig. 5 Pd-CATHODE, Pt-ANODE, D2O SYSTEM
VOLTS 5.0, CURRENT 0.5-0.8 A

Expt. No. 3

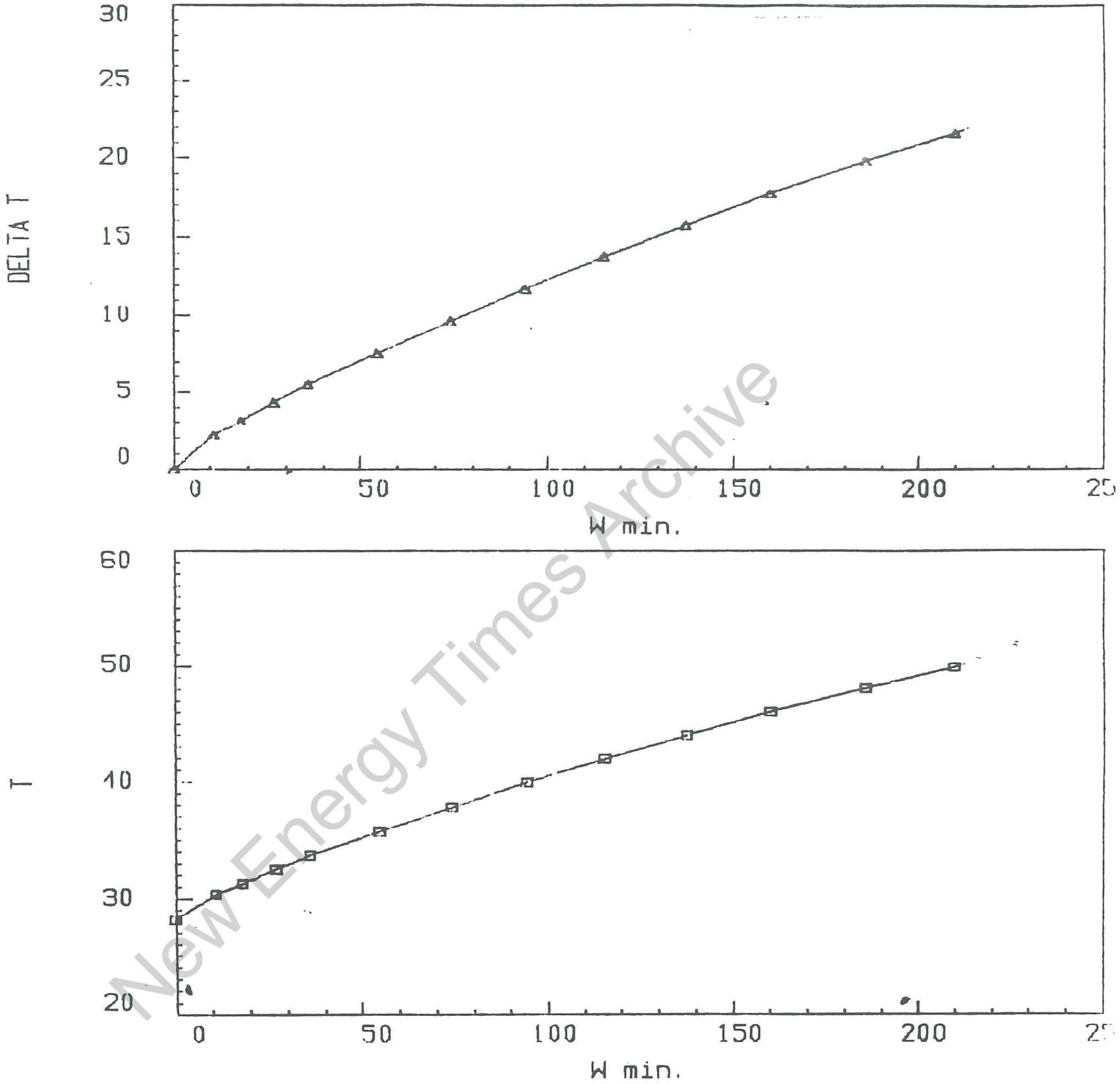


Fig. 6 PT--CATHODE, Pt--ANODE, D20 SYSTEM
VOLTS 5.5, CURRENT 0.45-0.60 A

Expt. No. 4

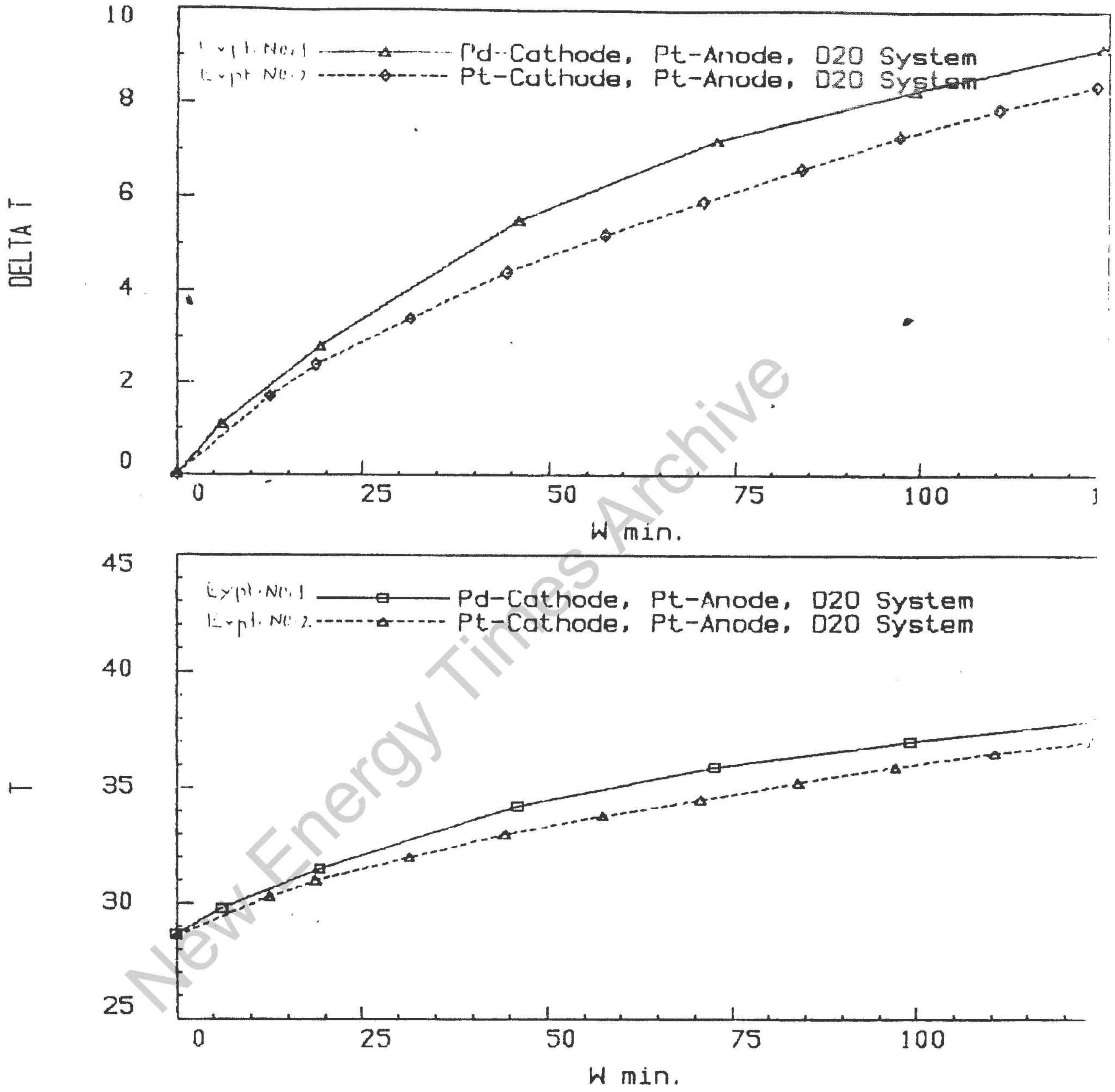


Fig 7. Data from Expts No 1 & 2 are superimposed,

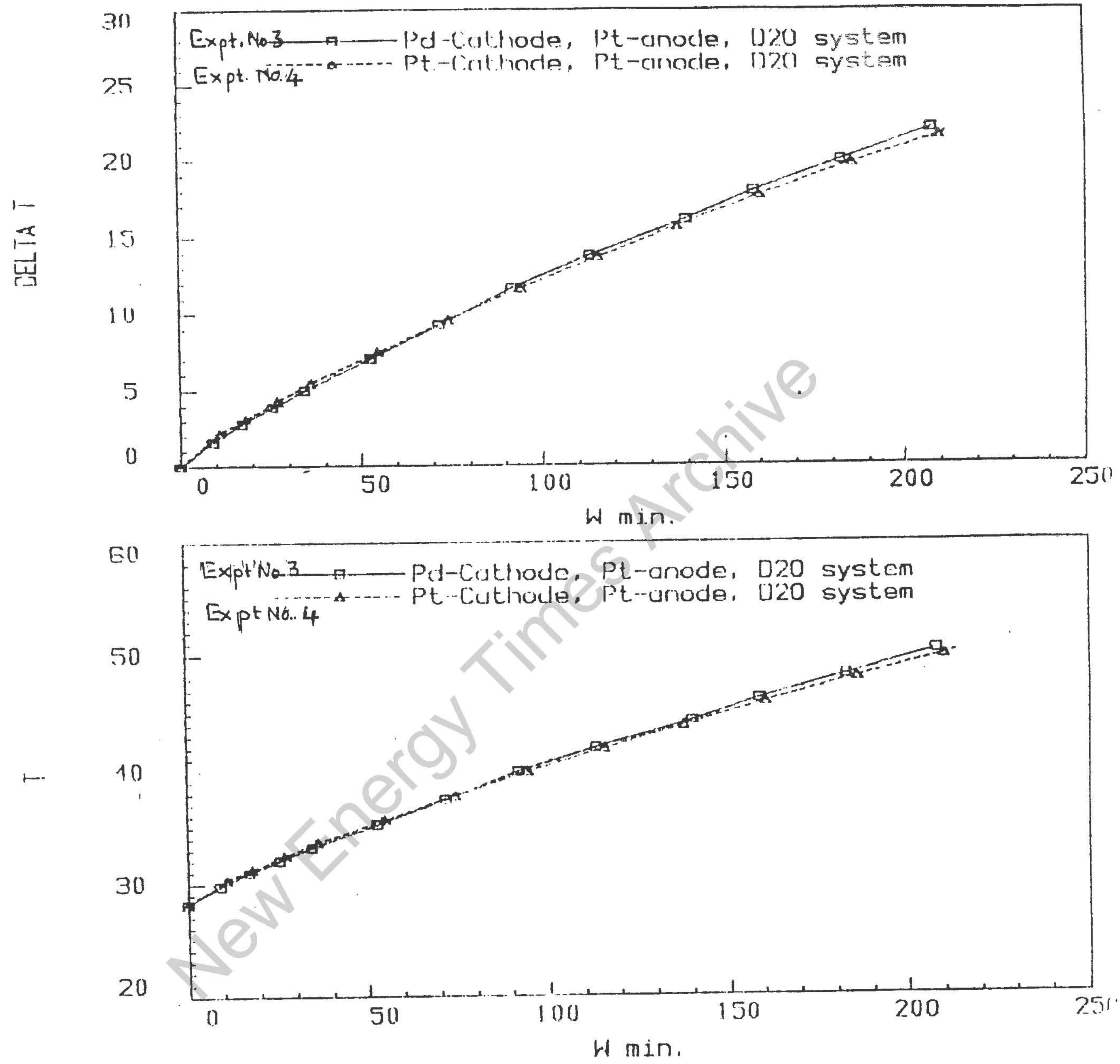


Fig. 8. Data from Expts No 3 and No 4 are superimposed.

The heavy water from the electrolytic cell was sent for tritium analysis elsewhere. It has been reported by oral communication that it contained tritium higher than the blank.

Conclusions :

Excess heating reported by Pons & Fleischmann in the electrolysis experiments of ;heavy water with palladium cathode was not observed in our experiments which were carried out in almost similar conditions. Instead of direct calorimetric measurements, the Pd–D_2O system was compared with Pt–D_2O system. It may be noted that the experiments were carried out for a maximum duration of 285 minutes during which temperature equilibrium conditions were not attained. Effects of deuterium loading on palladium if any, leading to cold fusion as a function of time, was not considered in these experiments.

Further work on cold fusion is in progress in a more systematic way with improved experimental conditions. A large size palladium (1 x 1 x 1 cm cube) cathode, a neutron counter, spacing of electrolyte solution with a suitable gas etc. have been employed in the new experiment. Results of this experiment will be reported soon.

Part II: Neutron Burst Measurements (16th to 22nd June 1989)

Introduction

The initial experiments, the results of which are reported elsewhere, were carried out with a small palladium tube and using lithium hydroxide with heavy water as the electrolyte. There was no indication of any excess heating in these experiments when compared with similar experiments using platinum as cathode in place of palladium. The present experiment was planned with improved experimental conditions for measurement of excess heat and emission of neutrons. Two major neutron bursts were observed. There was some evidence of excess heat in the cell from heat–transfer calculations based on the experimental data. Tritium measurements of the electrolyte were also made by taking samples from the cell during electrolysis. The results obtained in this experiment are discussed in this report.

Experimental

Palladium cathode : A palladium cube of dimensions 1 x 1 x 1 cm was procured from local suppliers. It was heated under vacuum to expel moisture and occluded gases. Electrochemical cleaning of the palladium cabe was carried out by making palladium as anode with respect to platinum cathode in an electrolyte solution of LiOD in D_2O. A current of 50 mA at 1.8V was passed through the solution for about 30 minutes.

Anode : It consisted of a split cylindrical platinum wire gauze surrounding the cathode.

Electrolyte solution : 0.1 M LiOD in D_2D. This was obtained by dissolving lithium metal in heavy water, having an isotopic purity of >99.86% w/w D_2O.
Weight of the electrolyte solution in the cell was 166 g.
Voltage supply to the cell : Electrolysis was carried out at constant current and variable voltage.

Temperature measurements : Cathode temperature was monitored by an MI thermocouple inserted in a cavity made on palladium surface. Temperature of the solution was measured using Pt–100 RTD placed in the solution. Both the temperatures were continuously recorded during electrolysis.

A mechanical stirrer operated by a mini DC motor was used whenever necessary for a thorough mixing of the electrolyte solution.

Gas aparging of the electrolyte solution was continuously carried out initially with nitrogen and later with helium and finally with deuterium gas.

Neutron Detector : A BF_3 neutron detector surrounded by paraffin wax was placed below the electrolysis cell. Its counting efficiency was 5 x 10^{-3} cps/fast neutron as obtained from a calibration using a standard neutron source at the location of the palladium cathode of the experimental set up. A pulse counting channel was connected to the neutron detector. The channel provided integrated neutron count display for a set time (selected for 300 seconds in this experiment) and counting rate signal for recording.

A resistance wire heater was placed in the cell to provide data on electrical heating without electrolysis. This data would be useful for comparison with that from Joule heating during electrolysis.

Photographs of the experimental assembly and the associated instrumentation are shown in Fig.1 and Fig.2 respectively. Schematic diagrams of the electrolysis cell and the associated instrumentation are given in Fig.3 and Fig.4 respectively.

Electrolysis was carried out initially at 600 mA corresponding to a voltage of 5.33 V which gradually dropped to 4.34 V after about 29 hours. The current was then raised to 700 mA for about 41 hours and the to 800 mA and the experiment was continued for a total period of 150 hours (which corresponded to 107.5 Ampere hours). Initially cylinder N2 was passed through the solution. This was changed to helium to eliminate oxygen present as an impurity in cylinder N_2. Subsequently D_2 was chosen for sparking since it would enhance the deuterium absorption in the palladium cathode. The composition of the cover gas in the cell was also determined occasionally to observe the D_2 content. Fresh heavy water was added to the cell from time to time (~53 ml total) to make up the losses caused by electrolysis, sampling and evaporation. Important observations made on neutron emission during the experiment and a summary of the experimental conditions such as gas used for purging, composition of cover gas, cell parameters, etc are given in a chronological order in Table 1.

The electrolyte solution developed colouration towards the end of the electrolysis. This was found to be due to corrosion of stainless steel surfaces of stirrer and RTD. This needs to be avoided in future experiments.

Discussion

Neutron Emission : During the progress of electrolysis, the BF_3 neutron counter indicated several neutron bursts as given in Table 1. Fig.5 and Fig.6 show two major neutron spikes observed on the first day of electrolysis, each lasting for about 45 min. and 60 min. respectively. These neutron signals corresponded to about 1 x 10^6 and 2.6 x 10^6 neutrons respectively. Besides these two spikes, there were five more. Since two of these lasted for very short duration, it is not clear whether they were genuine.

Cell Temperature and Excess Heating : The temperature of the electrolytic cell increased during electrolysis and stabilised as shown in Fig.7. The cathode temperature was a degree or two higher that that of the electrolyte solution throughout the experiment. The observed cell temperature data was used to assess the heating characteristics of the cell using a simplified heat–transfer analysis. This is described in more detail in the Annexure. This analysis was carried out for two cases corresponding to two conditions of the experiments as follows

Case A: 4.5 V; 600 ma; stabilized temperature 50.6° C.
Case B: 4.8 V; 800ma; 65.0° C

Table 1

Observations on Neutron Emission and Summary of Experimental conditions in a chronological order

Date	Time (Hours)	CPS (Recorded by BF_3 Counter)	Purge Gas	D_2 and O_2 in cover gas % v/v	Cell Temp. (° C)	Remarks
15.06.89	0845 - 1730	0.05	-	-		Cirus shut down
	1730	0.15	-	-		Cirus 40 MW
16.06.89	1055	0.15	N_2	-	28.0	Electrolysis started; Current increased in steps.
	1205	0.15	N_2	-	28.0	Cell voltage 5.33 V; Current 600 mA
	1245 - 1330	6.0	N_2	-	34.0-38.8	Neutron burst (1)
	1415	0.15	N_2	D_2 10.4 O_2 26		
	1452 - 1457	13	N_2	-		Sharp rise in CPS and cell temperature. (45°C → 55°C); Neutron burst ?
	1620	0.15	N_2	D_2 9.0 O_2 23.0	48	
	1725 - 1825	18	N_2			Neutron burst (2). Cathode temp. 52°C; Cell temp. 49.2°C
	1740	2	N_2	D_2 0.1 O_2 20.0		
	1816 -	0.15	N_2		49.5	
17.0689	0940	0.15			53.0	
	0940 - 1030	1	N_2		53.0	Neutron burst (3)
	1207 - 1220	0.6	N_2	D_2 35.0 O_2 21.0	53.2	Neutron burst (4)

...2

Date	Time (Hours)	CPS (Recorded by BF_3 Counter	Purge Gas	D_2 and O_2 in cover gas % v/v	Cell Temp. (° C)	Remarks
17.06.89	1230	0.15	N_2			
	1255 - 1331	0.05	N_2			Power failure; interruption in electrolysis; Cirus shut down.
	1331 - 0415	0.15	N_2			Electrolysis started; Cirus at 40 MW.
	1630	0.15	N_2		48.1	Cell voltage 4.6; Current 700 mA
18.06.89	0415 - 0450	0.8	N_2		54.0	Neutron burst (5).
	0700	0.15	N_2			D_2O added to the cell (20 ml)
	0930	0.15	He		55.5	
	1742	5	He		57.0	Sharp rise in CPS and cell temp. (57°C ⟶ 100°C; Neutron burst ?
19.06.89	0255 - 0930	1.2 (Steady)	He	D_2 55.9 O_2 25.3	56.0 56.0	Interference from Cirus (Tray rod work)
	0930	0.15	He		56.0	Cell voltage 4.89; Current 800 mA
	1020	0.15	He			Sample (6.2 ml); Electrolyte added (6.2 ml); D_2O added (7.9 ml)

...3

Date	Time (Hours)	CPS (Recorded by BF_3 - Counter	Purge Gas	D_2 and O_2 in cover gas % v/v	Cell Temp. (°C)	Remarks
20.06.89	1200	0.1	He	D_2 30 O_2 14	59.9	Cell voltage droppe by itself to 4.4 V; Current 630 mA
	1348	0.1	He			Current raised to 800 mA; Cell voltage 4.9 V
	1825	0.2	He			D_2O added (20 ml); Cell temp. (62°C → 59°C)
21.06.89	1000	0.05	He	D_2 7 O_2 8	65.0	Cirus shut down. Sample (7.5 ml); Electrolyte added (7.5 ml)
	1120	0.05	He			D_2O added (11.5 ml)
	1452	0.05	D_2		62.0	
22.06.89	0945	0.05	D_2	D_2 68 O_2 30	68.0	
	1515	0.05	D_2			Cell current was reduced in steps
	1620	0.05	D_2		60.0	Electrolysis terminated.

---oooOOOooo---

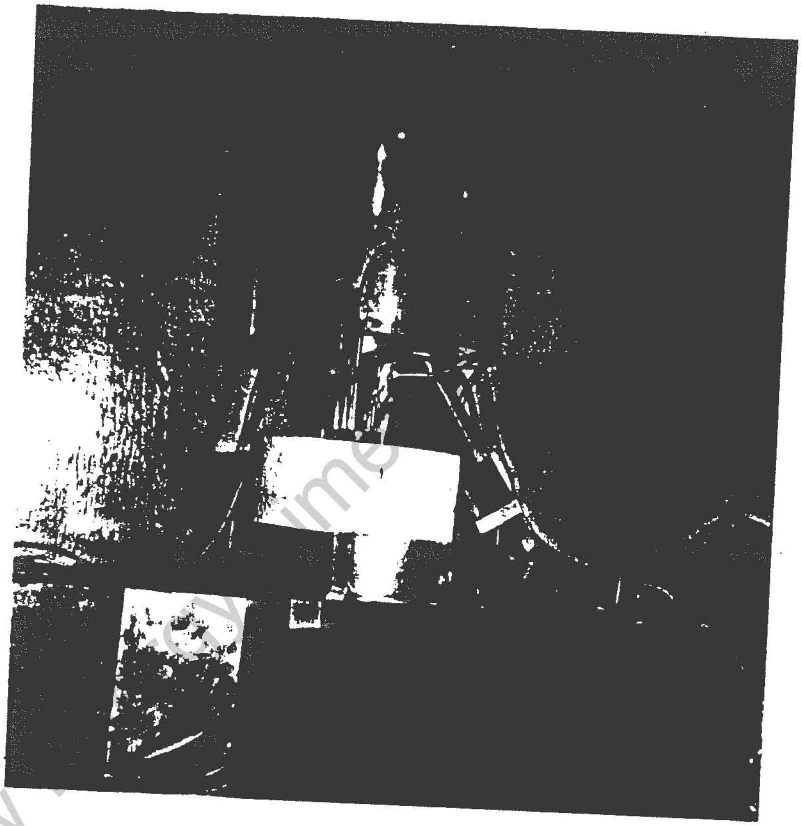


FIG. 1 - EXPERIMENTAL ASSEMBLY FOR ELECTROLYSIS

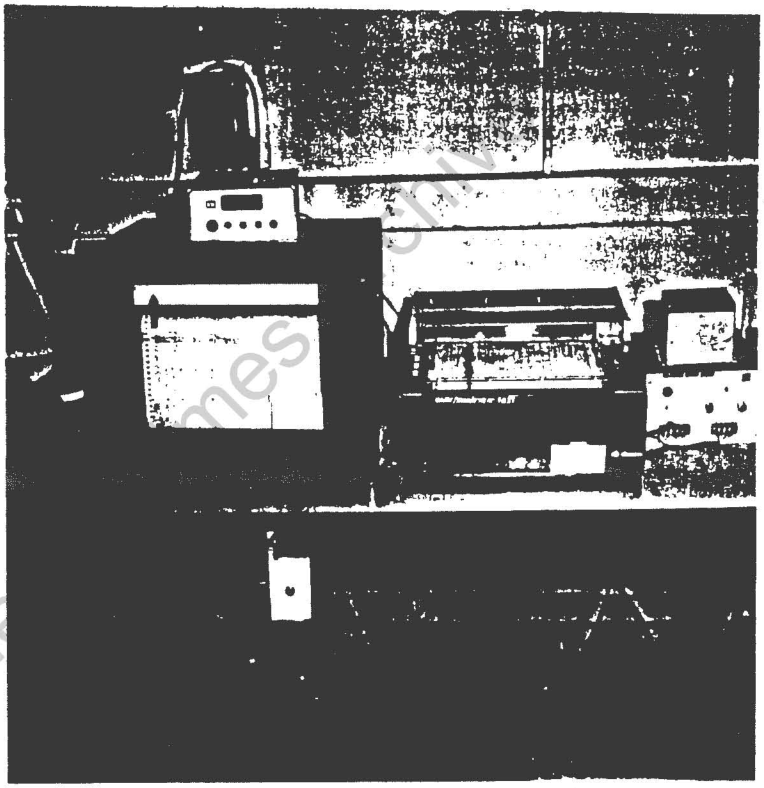
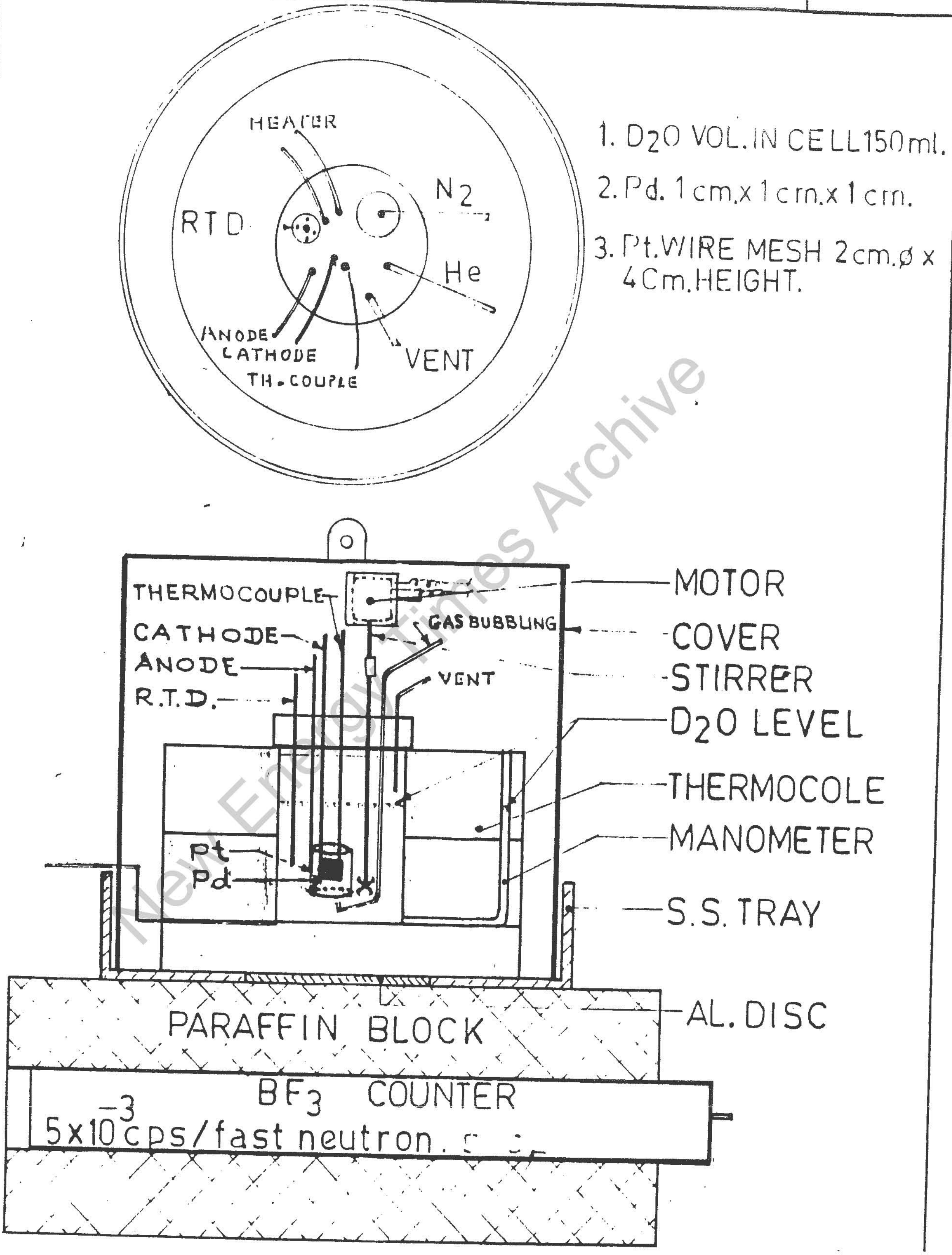


FIG. 2 - ASSOCIATED INSTRUMENTATION FOR NEUTRON AND TEMPERATURE MEASUREMENT DURING ELECTROLYSIS

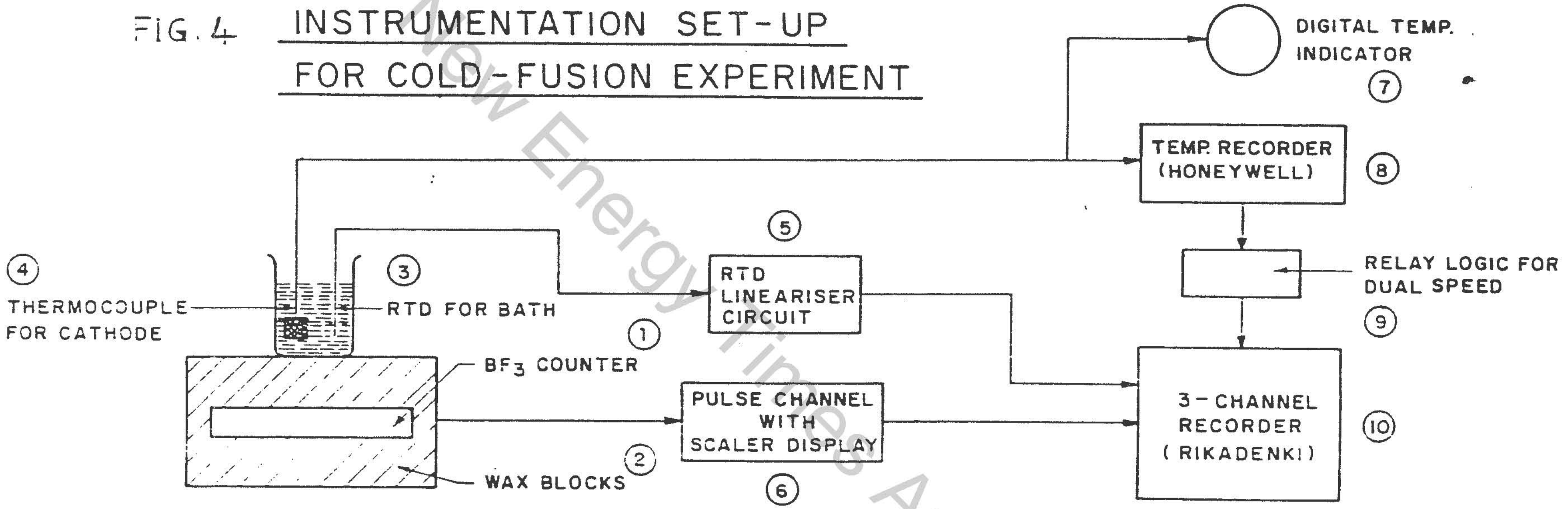
PROJECT	TITLE	REFERENCE
	COLD FUSION SETUP	



1. D_2O VOL. IN CELL 150 ml.
2. Pd. 1 cm. x 1 cm. x 1 cm.
3. Pt. WIRE MESH 2 cm. ø x 4 Cm. HEIGHT.

FIG. 3. CELL FOR ELECTROLYSIS

FIG. 4 INSTRUMENTATION SET-UP FOR COLD-FUSION EXPERIMENT


DIGITAL TEMP. INDICATOR
⑦
TEMP. RECORDER (HONEYWELL)
⑧
④
THERMOCOUPLE FOR CATHODE
③
RTD FOR BATH
⑤
RTD LINEARISER CIRCUIT
RELAY LOGIC FOR DUAL SPEED
⑨
①
BF$_3$ COUNTER
PULSE CHANNEL WITH SCALER DISPLAY
3-CHANNEL RECORDER (RIKADENKI)
⑩
②
WAX BLOCKS
⑥

① BF$_3$ COUNTER FOR NEUTRON COUNTING HAVING SENSITIVITY OF ABOUT 60 COUNTS PER Sec./NEUTRON FLUX.

② WAX BLOCKS FOR THERMALISING NEUTRONS.

③ Pt-100, 3 WIRE R.T.D. FOR MEASURING ELECTROLYTIC BATH TEMPERATURE.

④ MINERAL INSULATED, UNGROUNDED TYPE-T THERMOCOUPLE IN 3·2 mm. DIA. S S SHEATH, TIP EMBEDDED IN PALLADIUM CATHODE.

⑤ LINEARISER BRIDGE CIRCUIT, CONNECTED TO R.T.D., TO CONVERT 0-100 °C TO 0-100 mv OUTPUT.

⑥ PULSE COUNTING CHANNEL HAVING SCALER/TIMER DISPLAY FOR NEUTRON COUNTS AND 0-10V OUTPUT FOR 0·1 TO 10^5 cps.

⑦ DIGITAL TEMP. INDICATOR, CONNECTED TO THERMOCOUPLE.

⑧ HONEYWELL TEMPERATURE RECORDER, FOR CATHODE TEMPERATURE (0 TO 400 °C)

⑨ RELAY LOGIC TO PUT "RIKADENKI" RECORDER ON FAST SPEED (FOR 10 MINUTES) WHEN CATHODE TEMP. EXCEEDS 125 °C

⑩ 3 PEN-"RIKADENKI" RECORDER TO RECORD
i) NEUTRON COUNTS FROM 0·01 cps TO 10^4 cps AND
ii) BATH TEMP. FROM 0 TO 100 °C

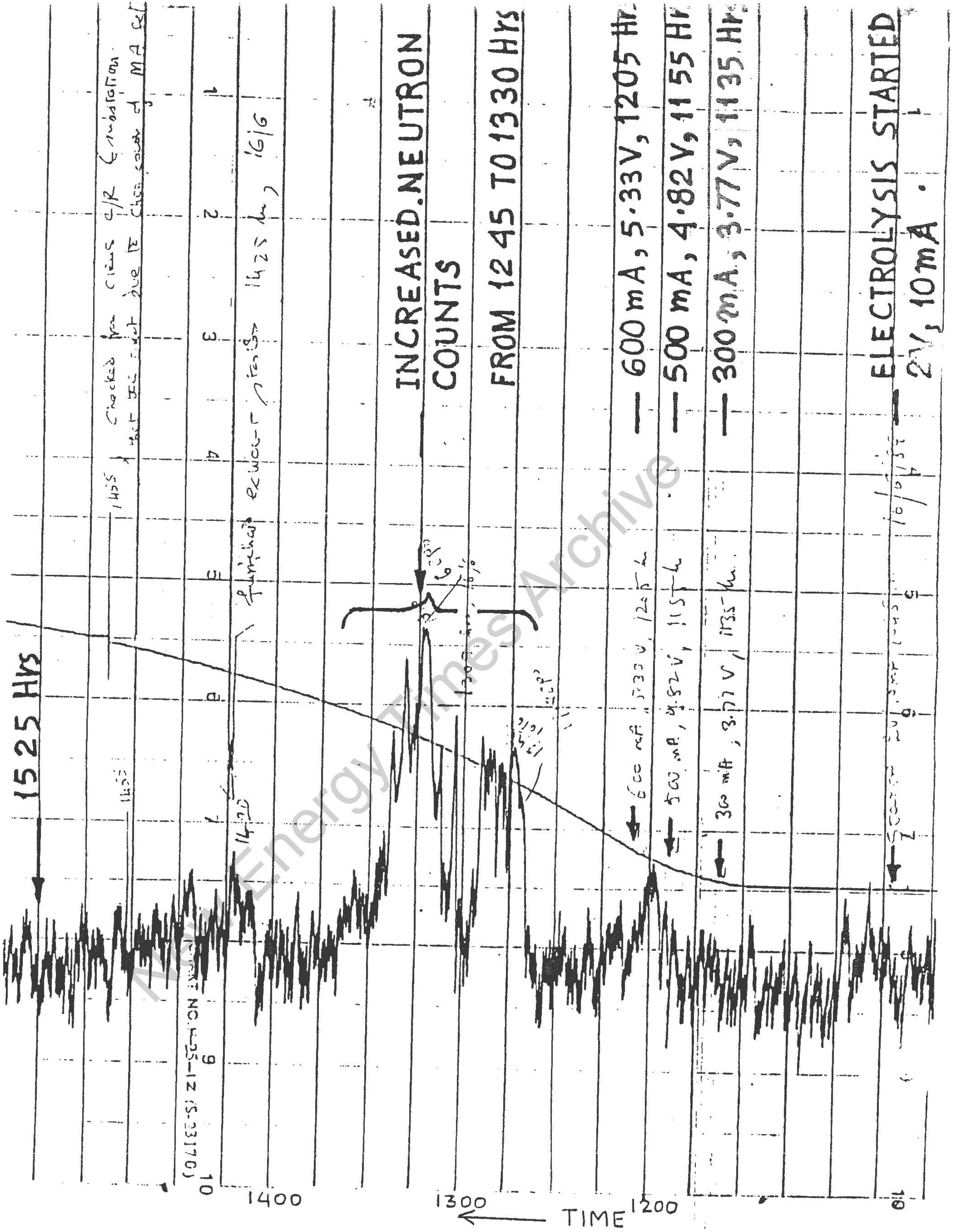


FIG. 5. NEUTRON SPIKES vs TIME

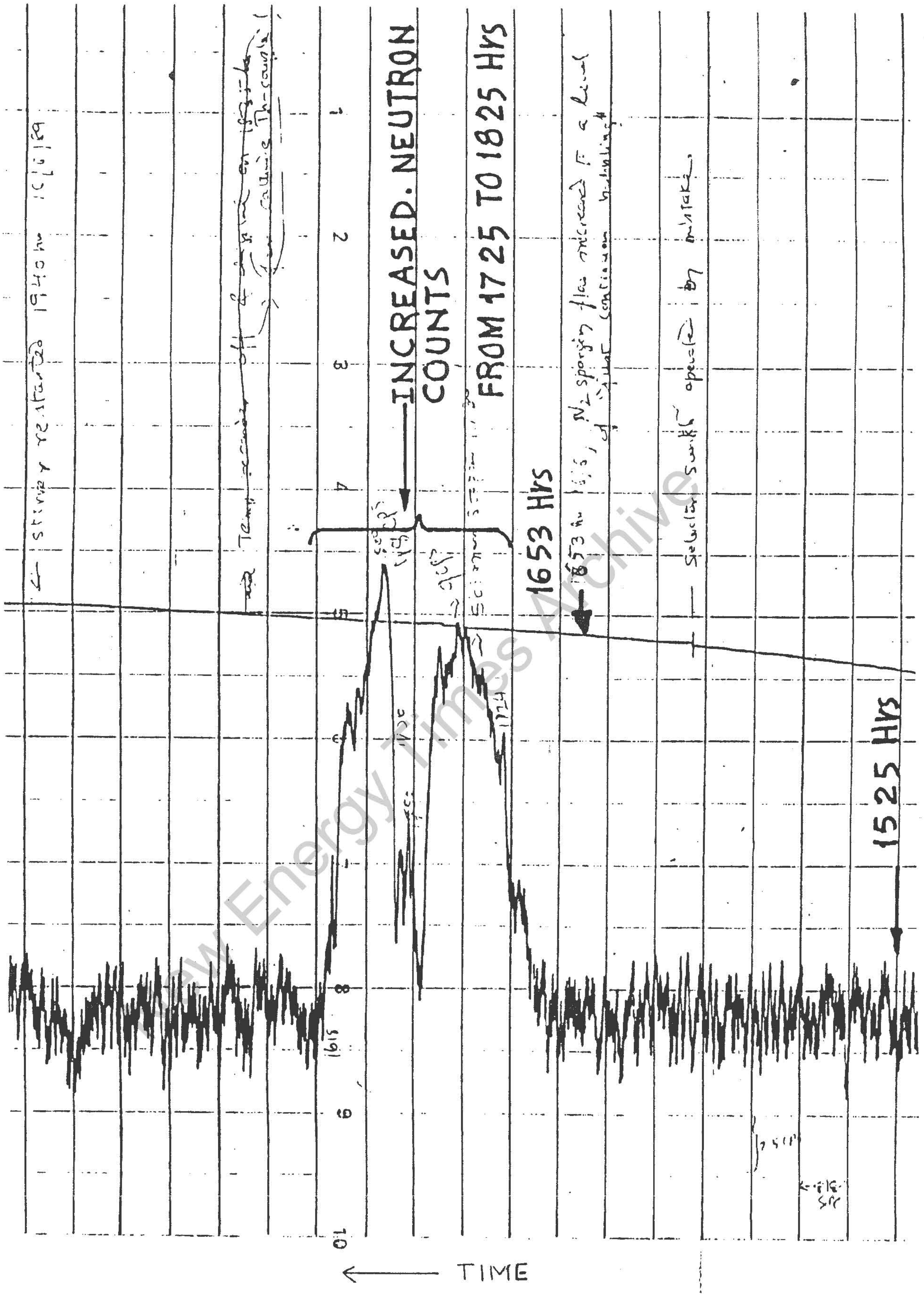


FIG.6. NEUTRON SPIKES vs TIME

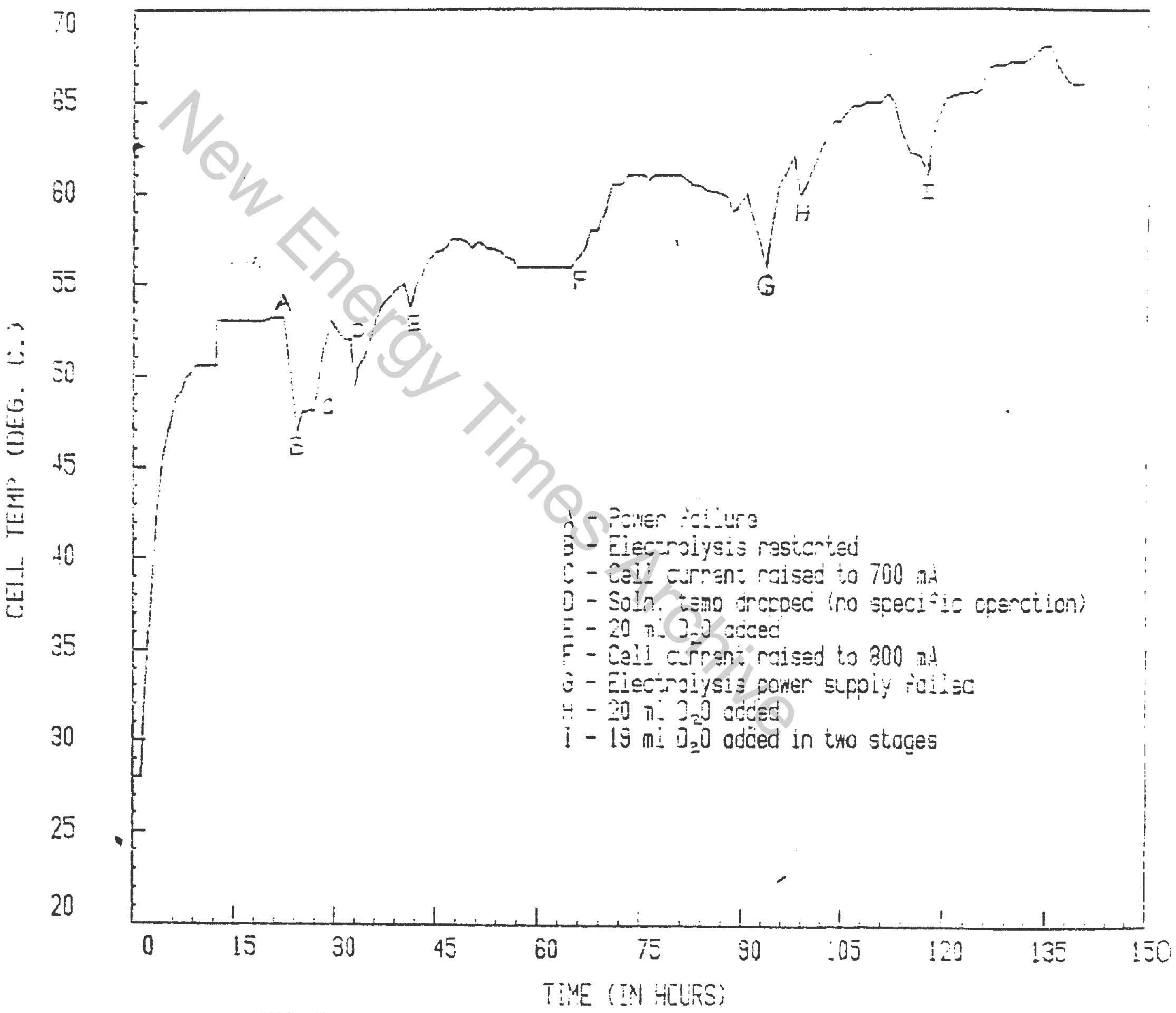


FIG. 7. - CELL TEMPERATURE VS TIME OF ELECTROLYSIS.

RCMG cold fusion experiment No 1 with Pd 1x1x1cm in room 41, CIRL's

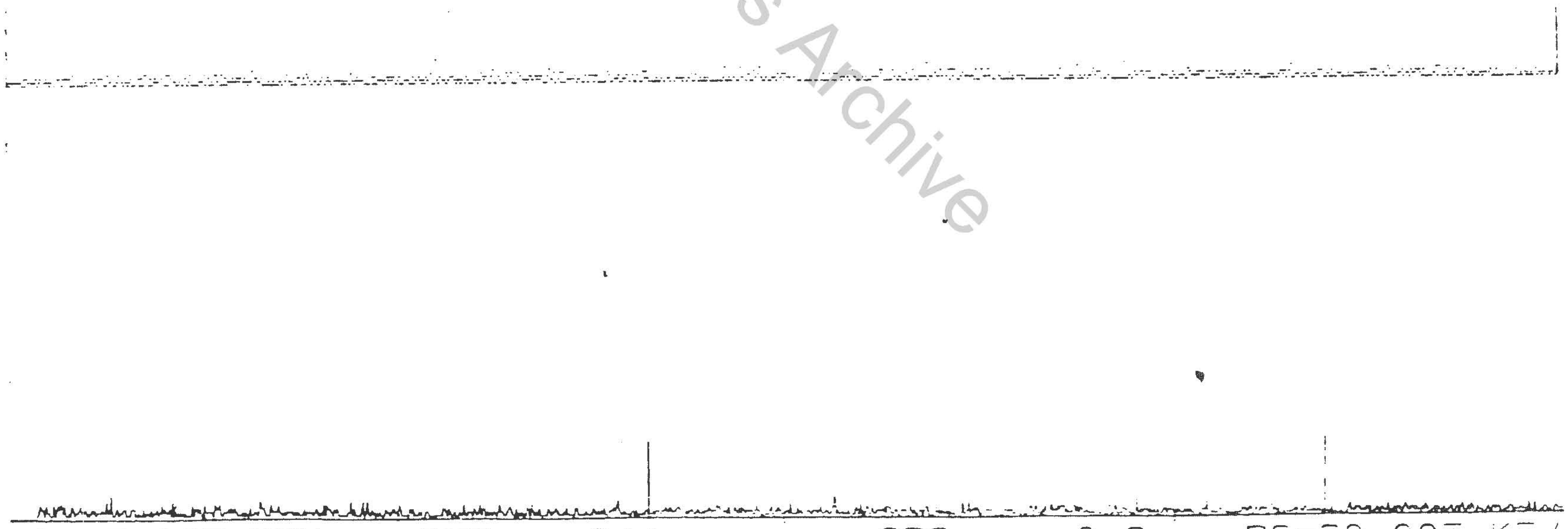
16 6.89 to 22.6.89 Ampere-hours 107.5

Pd unloading commenced at 1515 hrs on 22 6.89 and completed at 1620 hrs.

TIME (L) = 3001
PSET (L) = 10000

17: 55 22 JUN 89
UNIT# 1 DT= 0%
TAG NO. = Pd(1x1x1cm)0

15.005 KEV VFS= 128 CRT= (01-08) 30.005 KEV
CANBERRA



LC=15.005 KEV INT = 844 CPS = 0.2 RC=30.005 KEV
0 @LC 1 @RC

FIG 8 Pd K-SHELL X-RAY RECORDING

The thermal time constant of the system was determined from the experimental data. Using the time constant, water equivalent of the cell, and the observed stabilized temperature rise (with respect to ambient), the heating rate of the cell was computed. This was found to be 2.47 W for Case A. Based on the heat transfer analysis and observed temperature rise in Case A, the expected stabilized cell temperature rise in Case B was computed to be 29.7° C. However, the observed temperature rise in Case B was 37° C. Heating rate estimated from the experimental data in this case was 4.05 W.

It can be seen from the calculations in the Annexure that the Joule heating for Case A and Case B are 1.5 W and 2.28 W respectively. Thus, the results obtained from the heat–transfer analysis seem to indicate excess heating of 0.97 W for Case A and 1.77 W for Case B. However, these excess heating values are smaller than the estimated lower limit values of 3.8 W and 5.2 W for Case A and Case B respectively interpolated from the excess heating data on cold fusion reported by Pons and Fleishmann in their paper (J. Electroanal. Chem. 261, p 301, 1989).

The palladium cube, after 150 hours of electrolysis, was counted for 21 KeV Pd–K–shell X–rays that might have been excited by protons produced via the nuclear reaction D + D ——T + p. A chart recording for this counting is given Fig.8. There was no positive indication for the Pd–K–shell X–ray emission.

The cell heavy water samples were sent for tritium analysis. The results will be reported elsewhere.

Conclusions :

The present experiment has given evident for neutron emission and possible excess heating arising from reported cold fusion. Tritium results would throw further light on the observed phenomenon.

During electrolysis, the liberated gases D_2 and O_2 may recombine in presence of palladium (acting as a catalyst) producing heat. It is assumed that palladium which was inside the electrolyte solution would not catalyse such a reaction. Also, above the solution, such a reaction is believed to be not significant due to absence of a suitable catalyst.

During degassing of the palladium cube on heating under vacuum for use in the next experiment, it was observed that a lot of accumulated gases continued to evolve for almost an hour.

Experiments are being planned to collect additional data on the subject.

Part III: Analysis of Observed Cell Temperature Variations

Introduction

In a typical run of the experiment (Case–A) conducted on June 16, 1989, a cell voltage of ~4.5 volts and a constant cell current of ~600 mA were used and the neutron count rates and the electrolyte as well as the palladium cathode temperatures were monitored periodically. The stirrer was intermittently operated during these measurements.

Subsequently another experiment (Case–B) was carried out with a call voltage of ~4.85 volts and a constant cell current of ~800 mA.

Table—1 summarises the temperature variations observed till the system reached equilibrium.

Since it is complex to arrive at the heat transfer conditions of the system from first principles, the observed time variation of the cell temperatures in the Case—A experiment (4.5V, 600 mA) were used to obtain the thermal time constant o the system. Using the known water equivalent value (W) of the major contents of the cell, the effective product of the heat transfer coefficient to the ambient heat sink and the heat transfer area of the system (hH) eff for this experiment was estimated. Finally the cell heating rate (Pcell) is obtained as the product of (hA) eff and the observed stabilised temperature rise of the cell with respect to the ambient temperature. This 'observed' cell heating rate was compared with the expected cell joule heating for the voltage and current values used for the experiment.

Based on the above approach, an assessment was also done for the expected stabilised cell temperature for case—B experiment (4.85 V, 800 mA) for comparison with the observed value.

Finally the expected cell temperature variations with time were assessed for the heat transfer conditions of the experiment, but assuming ;that the cell heating is due to
a) only the joule heating,
b) joule heating plus an estimated lower value of the cathode heating due to cold fusion events and
c) joule heating plus an estimated upper value of the cathode heating due to cold fusion events.

The cathode heating rates were estimated using an approximate formula obtained by fitting the experimental data given by Stanley Pons and Martin Fleishmann.

Cell Heat Transfer Analysis

For a system with a heating source P, water equivalent W, heat transfer area A, effective heat transfer coefficient to ambient heat sink h, and ambient sink temperature Ts, the volume average system temperature T, will be given by

$$W\frac{dT}{dt} = P - h.A.\,(T-T_s) \qquad (1)$$

With the assumption that initially the cell and the heat sink temperatures are different and that the heat sink temperature does not vary with time, the solution of equation (1) with the scale of $T_s = 0$ is given by

$$\Delta T(t) = \Delta T\,(0)e^{-t/\tau} + \Delta T\,(\infty)\,(1-e^{-t/\tau}) \qquad (2)$$

where $\Delta T\,(t) = P\,/\,(hA)$ and $\Delta T\,(t)$ is the excess of cell temperature at time 't' over the sink temperature T_s and

$$\tau = W\,/\,hA \qquad (3)$$

where τ is the effective system thermal time constant.

Assuming that initially the cell and heat sink temperatures are equal, the cell thermal time constant can be approximately estimated from equation (2) using the derived relation

$$\tau \; = \; t/\mathrm{Log}_e\left\{\frac{\Delta T(\infty)}{\Delta T(\infty) - \Delta T(t)}\right\} \qquad (4)$$

The observations for the Case–A experiment given in Table–1 were used to estimate the thermal time constant. The mean value from different data works out to be about 2.04 hour, for the cold fusion experimental set up in the Reactor Chemistry Section Laboratory (Room No. 41, Cirus).

It may be noted that theoretically the stabilised cell temperature (excess over heat sink temperature) is directly proportional to the cell heating rate Pcell (for given set up and heat transfer conditions).

Thus the assessed cell heating 'Pcell' for the Case–A experiment can be worked out using the observed stabilised cell temperature rise using

$$\mathrm{Pcell} = \Delta T(\infty) \times (\mathrm{hA})\,\mathrm{eff}$$

and

$$(\mathrm{hA})\,\mathrm{eff} = W/\tau \qquad (5)$$

Note : This calculational model has been verified to yield satisfactory results (within about 10%) when typical cell contents were heated by electrical resistance heaters with known heating. For the details of this calibration testing, please see Appendix–I attached.

For the cell used for the experiments, the estimated water equivalent is W = 191.4 cal / degC as given below :

Major component (Cal/degC)	Mass (g)	Sp.ht	Water Eq.
Glass Beaker	125	0.1988	24.85
Heavy Water	165	1.0	165.0
1cm cube Pd	11.4	0.061	0.695
Pt Anode	26	0.33	0.858
		Total	191.4

Thus (hA) eff = 191.4/2.04 = 93.8 Cal/hr/degC

Since $\Delta T(\infty)$ observed is 22.6 degC for the (4.5V, 600mA) experiment,

$$\mathrm{Pcell} = \Delta T(\infty) \times (\mathrm{hA})\,\mathrm{eff} = 22.6 \times 93.8\ \mathrm{cal/hr}$$
$$= 2120.4\ \mathrm{cal/hr} = 2.47\ \mathrm{watts}$$

The assessed value Pcell for the experiment may be compared with the expected cell joule heating Pj responsible for heating the cell contents (in the absence of any additional heating produced by possible "cold fusion" events in the palladium cathode).

$$\mathrm{Pj} = (\mathrm{Vcell} - \mathrm{VO}) \times \mathrm{Icell} = (4.5 - 2) \times 0.6$$

= 1.5 watts

where Vcell is the cell voltage applied, Icell is the cell current and Vo is the thermoneutral potential for the cell (upto which no cell current is possible).

The value of Vo for the cell used was experimentally found to be Vo = 2 volts.

Thus the observed incremental change of system stabilised excess temperature over heat sink temperature for the cell leads to a value of 22.6 / 2.47 degC/Watt = 9.1 degC/Watt.

Comment :

It may be noted that the assessed cell heating (2.47 watts) purely from the (4.5V, 600 mA) cell experimental data is LARGER (by about 0.97 watts) than the expected cell joule heating (1.5 watts). This conclusion is significant. However before attributing this discrepancy to cold fusion events in the palladium cathode, it is worthwhile to eliminate/minimise all unwanted heat inputs to the cell such as that due to the electrical stirrer and to accurately know the cell joule heating and repeat the experiment carefully.

Using the above approach one can also assess the expected cell equilibrium temperature for the Case–B experiment conducted on 20–6–89 with the same experimental set up used for the Case–A experiment. In this case the cell temperature stabilised at 65^{0}C with an ambient of 28 C, leading to a cell temperature rise of 37^{0}C.

However assuming the heat transfer parameters assessed for the Case–A experiment are applicable for Case–B experiment, one would expect a cell temperature rise of

$$(22.6 / 2.47) \times [(4.85 - 2) \times 0.8 + (2.47 - 1.5)] =$$

$$(22.6 / 2.47) \times [\, 2.28 \text{ watts} + 0.97 \text{ watts} \,] = 29.7 \text{ C}$$

to be compared with the observed value of 37^0 C.

The assessed cell heating using the observed stabilised cell temperature rise works out to be 37^{0}C x 93.8 = 3471 Cal/hr = 4.05 watts. for the Case–B experiment. It may be noted that the additional heating of 0.97 watts observed over the estimated joule heating of 1.5 watts in the Case–A experiment is already corrected for in this assessment.

Comment :

Thus the assessed cell heating (4.05 watts) is also LARGER than the expected joule heating of 2.28 watts in the cell experiment with (4.85 V, 800 mA). Anticipated cell temperature variation with time for the assumed palladium cathode heating due to cold fusion events. To compare the observed cell temperature variations with time with the expected values if the palladium cathode has heating due to cold fusion, calculations were done using equation (2). An approximate value for the cathode heating was obtained using a least square fitted relation as a double conic function of palladium cathode rod diameter and cathode current density.

$$Q = 0.00855 \times D^{0.364} C^{1.13}$$

where Q = Excess heating rate in Pd cathode (W/cc)

D = Pd rod diameter (mm)

and C = Cathode current density (mA/sq.cm)

The palladium cathode excess heating rate data given by Stanley Pons and Martin Fleishmann [in their original paper "Electrochemically induced nuclear fusion of Deuterium", J. Electroanal Chem, 261 (1989)] were used for this fitting. The fit has a standard deviation of 18.3% for the nine data used as given below. For each value of Pd diameter, the first line gives the reference data and the second line gives the fitted value, as a function of the cathode current density.

Pd Rod Dia	Excess Heating Rate (W/cc) for Current density 8 mA/sqcm	64 mA/sqcm	512 mA/sqcm
1.0	0.095	1.01	8.33
	0.089	0.93	9.70
2.0	0.115	1.57	9.61
	0.115	1.20	12.5
4.0	0.122	1.39	21.4
	0.148	1.54	16.1

The equivalent rod diameter of the 1 x 1 x 1 cm cube of palladium used is 11.28 mm. The current density would be in the range of 100–111111150 mA/sqcm for Case–A and in the range of 1333–200 mA/sqcm for Case–B.. Using the fitted relation, the estimated lower limit excess heating in the cathode are 3.76 W/cc and 5.19 W/cc for Case–A and Case–B respectively. The corresponding upper limit values are 5.94 W/cc and 8.23 W/cc for the two cases.

For Case–A experiment, calculations were done using equation (2) for the anticipated cell temperature variation with time for the lower and upper limit values of the excess heating in the cathode in addition to the estimated joule heating of 1.5 Watts. The heat transfer condition was assumed to be characterised by the estimated thermal time constant of 2.04 hour and by the (hA) eff value of 93.8 Cal/h/degC.. The computed upper and lower limit stabilised cell temperatures are 48.1 C and 68.0 C. Figure 11.1 gives the results. For comparison, curves for only joule heating of the cell and the actually observed temperatures (for assessed cell heating of 2.47 watts) are also indicated in Fig–1.1.

Comment:
It is seen that the observed cell temperature variations with time are much lower than those anticipated with estimated excess heating in the cathode. However they are significantly higher compared to the cell condition with only calculated joule heating present. Thus additional experiments with carefully controlled heat transfer conditions and higher values of cathode current density than that used in Case–A would be worthwhile.

Recommendations
Since both the Case–A (4.5 V, 600 mA) and Case–B (4.85 V, 800 mA) cell experiments seem to indicate larger than expected (joule) heating in the cell, it is

worthwhile to repeat the cell experiments carefully with:
(i) unwanted (but accurately known) heat inputs into the cell eliminated/minimised,
(ii) avoiding thermal contacts of the beaker surfaces with surrounding structural metal components (if any) so as to facilitate accurate estimation of cell water equivalent value and
(iii) increased cathode current density values at reduced cell voltages to minimise joule heating for easier resolution of the excess cell heating due to cold fusion events if they occur. Closely spaced cylindrical geometry electrodes and increased electrolyte electrical conductivity values may be helpful in this regard.

Run of (June 16, 1989)

Observations with Resistance Heating of the Cell

Calculations were also done for a simulation cell experiment carried out on 23.6.89, in which the cell contents were heated by electrical resistance heating, aimed to simulate the experimental conditions used for case–A and Case–B experiments. The heat input to the cell was known from the voltage and current values and the actual fraction of the resistance wire immersed in the electrolyte used for resistance heating experiment.

During the resistance heating experiment, stabilised cell temperatures were noted for three different sets of cell voltage and current values, (viz.) (4.5V, 555 mA), (5.7V, 700 mA) and (6.4V, 780 mA).

The observed time variation of the cell temperature for the (4.5 V, 555 mA) was analysed using the "thermal time constant method".. The cell heating rates were then assessed for comparison with the heating values, known from current and voltage values used. It may be mentioned that, there was no electrolysis involved in these experiments.

Using the 'time constant' method the cell temperature variations with time for the simulation experiment with resistance heating were analysed. These observations are given in Table–1, and the estimated mean time constant value from different data was 3.62 hour. Thus the heat transfer conditions for the resistance heating experiment are not quite similar to those for case–A (for which a thermal time constant value of 2.04 hour was assessed from its experimental data). This is possibly due to the absence of electrolysis (and associated gas release phenomena) and due to changes in effective thermal environmental conditions of the cell, which could influence heat losses from the system used for the resistance heating experiment.

Following a similar procedure has for case–A, the cell heating value is assessed to be Pcell = 1.67 watts for the resistance heating experiment, to be compared with the actual heating value of 1.5 W, as given below:

$$(hA)\text{eff} = W/\tau = 191.4/3.62 = 52.9 \text{ cal/hr/C}$$

$$\Delta T(\ ) = 27^0\text{C (observed)}$$

$$\text{Pcell} = \Delta T_\infty)..(\ ) \times (hA)\text{ eff} = 27 \times 52.9$$

$$= 1428.3 \text{ cal/hr} = 1.67 \text{ Watts}$$

The actual cell heating value can be computed from the voltage and current values used for resistance heating and is given by

$$4.47 \text{ volts} \times 555 \text{ mA} \times (36.3/60) = 1.50 \text{ watts}$$

where the factor (36.3 cm/60 cm) represents the ratio of the resistance heating wire immersed in the electrolyte to the total length of the resistance wire used in the experiment. The additional correction factor due to a small length of the wire within the cell above the electrolyte level was experimentally found to be negligible.

Similarly the cell resistance heating values for the (5.7V, 700mA) and (6.4V, 780 mA) portions of the experiment were also assessed using estimated time—constant and the observed stabilised cell temperatures. These are tabulated below:

Voltage(V)	Current(mA)	Temperature	Cell Heat.	Time Const
4.5	555	27.0	1.67	1.50
5.7	700	40.5	2.50	2.41
6.4	780	46.1	2.85	3.02

The good agreement (within 10%) between the assessed cell heating value (using the thermal time constant method) and the actual resistance heating gives confidence for the application of the thermal time constant method for the cell experiments.

Fig-1.1 Cold Fusion Expt(Vcell=4.5V;Icell=600 mA)

Wat.Eq(Cal/°C)=191.4 ; Time Const(hr)=2.04

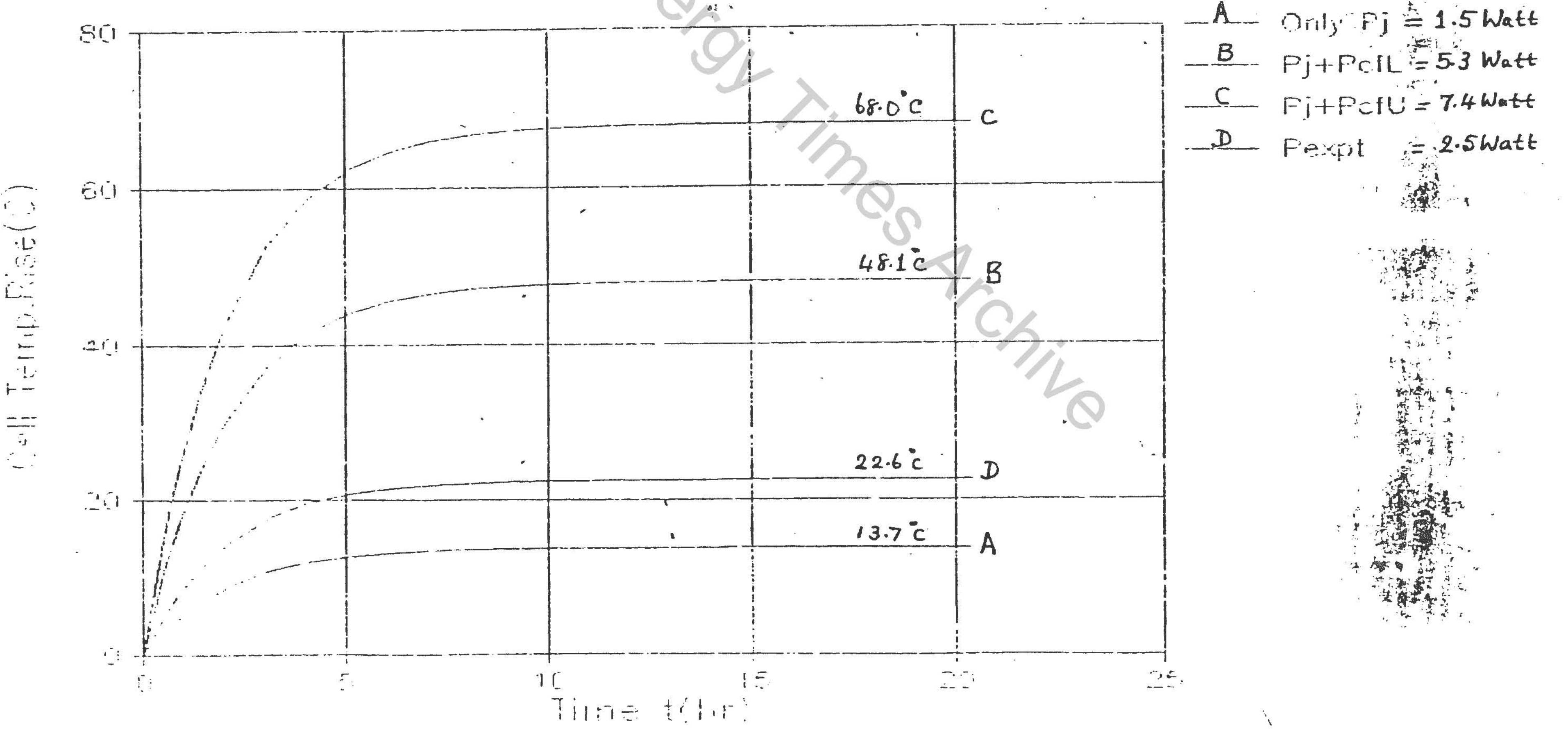


Table 1. Summary of Observations during Electrolysis

Experiment Case-A Date: 16-6-89			Ts(degC)=	28	
Time	Voltage (V)	Current (mA)	Pd temp (DegC)	Tcell (DegC)	Temp Rise (DegC)
1200	5.33	600	27.5	28	0
1415	4.79	600	44.5	42.8	14.8
1505	4.66	600	47	45.4	17.4
1600	4.58	600	48	47.2	19.2
1700	4.53	600	51	48.8	20.8
1755	4.51	600	52	49.2	21.2
1900	4.48	600	52	50.1	22.1
2000	4.5	600	52	50.6	22.6
2200	-4.45	600	53	50.6	22.6
2300	4.42	600	53	50.6	22.6

Av · 4.525v

Time	t (hour)	Temp Rise (DegC)	$Y = \frac{[T(inf) - Ts]}{[T(inf)-T(t)]}$	Thermal Time Cons= $\frac{t}{LnY}$ (hour)
1200	0	0	-	-
1415	2.25	14.8	2.897436	2.115007
1505	3	17.4	4.346154	2.041801
1600	4	19.2	6.647059	2.111738
1700	5	20.8	12.55556	1.976157
1755	6	21.2	16.14286	2.157127
1900	7	22.1	45.2	1.836741
2000	8	22.6		~~1.836741~~
2200	10	22.6	Av.Time Const =	2.039762
2300	11	22.6		

Table-1: Cold Fusion Experiments in ROMG(June 23, 1989)
(With 1 x 1 x 1 cm Palladium Cathode and
2 cm dia x 4 cm long Platinum Anode)
Resistance Heating Run

Experiment No. #1 Date: 23-6-89 Ts(DegC)= 26.5

Time	Voltage (V)	Current (mA)	Solution RTD	Temp(C) Th.Coup	Temp Ris (DegC)	Time Int t(hour)
1100	0	0	26.5	27	0	-
1115	0	0	26.5	27	0	-
1130	4.48	555	26.5	27	0	0
1230	4.47	555	33	34	6.5	1
1330	4.46	555	37.8	38	11.3	2
1430	4.46	555	41.5	42	15	3
1600	4.46	555	45.6	46	19.1	4.5
1800	4.47	555	49	50	22.5	6.5
2000	4.47	555	51.5	52	25	8.5
2200	4.47	555	52	52	25.5	10.5
0	4.48	555	52	53	25.5	12.5
200	4.47	555	53	53	26.5	14.5
400	4.47	555	53.5	54	27	16.5
500	4.47	555	53.5	53	27	17.5
600	4.47	555	53.5	53	27	18.5
700	4.47	555	53.5	53	27	19.5

Time Int t (hour)	$Y = \frac{[T(inf)-Ts]}{[T(inf)-T(t)]}$	Time Const (hour) $= \frac{t}{LnY}$
-	-	-
-	-	-
0	-	-
1	1.317073	3.630924
2	1.719745	3.688838
3	2.25	3.699455
4.5	3.417722	3.661591
6.5	6	3.661591
8.5	13.5	3.661591
10.5	18	3.661591
12.5	18	3.627719
14.5	54	3.265852
16.5		
17.5	Mean Time Const	3.617683
18.5		
19.5		

BARC Studies in Cold Fusion

Search for Nuclear Fusion In Gas Phase Deuteriding of Titanium Metal

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The possibility of D–D nuclear fusion in some deuterium–metal systems, under ambient conditions, has aroused feverish world wide interest. Most of the work reported, so far, concerns deuterium charging of Pd metal through electrolysis of D_2O.

In Chemistry Division, we have carried out some experiments on the deuteriding behaviour of Ti metal, through gaseous route, in the absorption as well as desorption modes, with the view to look for the fusion products,neutrons in the present case. This kind of experiments have been reported by Frascatti Group in Italy. These authors detected neutron emission lasting over a period of several hours.

Experimental

Experimental arrangement for deuteriding Ti metal is shown in Fig.1, which is self–explanatory. This set up has been routinely used for high pressure hydriding studies on several systems, reported by us (1–3). In some of the experiments reported here, deuterium pressure was cycled between high and low values by simply changing the temperature of the cell housing the sample. Most of the experiments were done in the desorption mode. Ti metal pieces (cut from a sheet) were surface cleaned and subjected to activation treatment before D_2 loading and subsequent desorption treatment etc.

Neutron counting set up consists of an array of 24 He^3 counters arranged in a well like geometry. These counters diameter (each 50 cm in length 2.5 cm in diameter and filled with He^3 at 4 atm.) housed in paraffin moderators, are all connected in parallel to a single pre–amplifier. The counting efficiency of this system was found to be 10%. The counts are recorded in 8192 channel multi–scalers. In the experiments reported here dwell time of 40 sec. was fixed, so that each point in Fig.(2) to (5) represents the number 4* of counts per 40 sec. The back–ground counts collected for about 10 days, before the start of these deuteriding experiments, was found to be quite steady 60 counts/4O secs. This back–ground count rate continues to be the same well after our experiments.

Results:

In the first set of experiments, starting from 3rd June 1989, after activating Ti metal pieces, D2 Gas was contacted with the sample at a pressure 10 atm. while keeping the sample at low temperature (~77K). After a soaking time of ~20 min., sample temperature was raised gradually, while simultaneous evacuation was started. Within about 15 min. the neutron counter registered an increase in count rate reaching a max. 3900 (as compared to back–ground counts of ~60), see Fig.2. On withdrawing the reactor from the counting well, a considerable reduction in the counts was observed. On re–introducing the reactor after background counts are restored, an additional peak like structure was observed. Although the evacuation was continued, no further increase in count rate over the background could be observed over the next twenty hours.

Next experiment on the same charge was carried out by repeating the conditions of first experiment. The results of this experiment, dated 4th June 1989, are shown in Fig.3. Again two peak like structures, each lasting for about 30 min. and separated by 50 min. were seen. However, the intensities of both these structures are greatly reduced, as compared to the first experiment (3rd June 1989), the max. Counts being ~.700)

In the third experiment, with the same charge of Ti pieces, D2 gas pressure was made to cycle between ~50 atm. to 13 atm. by changing the reactor temperature from room temperature to 77 K. In this case large changes in counts, temperature to 77 K. In this case large changes in counts, as a function of time were noticed. An increasing trend of counts initiated at ~2330 hrs on 4th 3 June 1989 lasted for almost 7 hrs. with an estimated integral counts ~$6.5x10^5$. Even after this long bursts like structures, some additional peaks were observed on 5th June 1989. With no further structures observed over the next few hours, desorption was carried out after loading the sample with D_2 has with the sample temperature at ~ 77K. By raising sample temperature gradually, while simultaneously evacuating, a much bigger structure lasting for ~2 hrs. (from ~1830 to 2030 hrs. on 7th June 1989) Was seen (Fig.4). An approximate estimate of integrated count over this period is $7x10^5$ Further experiments with this charge, involving D_2 loading followed by prolonged periods of evacuation at temperature upto a max. of ~200^0C,did not show further structures.

Second series of similar experiments on a fresh charge of Ti from the same source did not exhibit exactly similar behaviour, as found for the first charge. However, one set of experiments on 17th June 1989 (see Fig.5) involving pressure cycling, followed by evacuation, exhibited increase in count rate lasting over a period of ~100 min. In this case, the scatter in the counts was found to be rather large and maximum counts upto 10^5/40 sec. were observed, as compared to back–ground count of ~60/40 sec. This charge showed no further increase in count rate even after various treatments.

Further experiments are planned – (i) to study all possible parameters relating to the observed increase in the count rates,(ii) to identify the source of these extra counts, and (iii) to investigate the energy and time structure of the radiation responsible for the observed peak like structures.

Acknowledgement

Authors are thankful to Dr R.M. Iyer, Director, Chemical Group for encouragement and helpful discussions. Thanks are also due to Dr P.R. Natarajan, Head, Radiochemistry Division and his colleagues for providing neutron counting facility.

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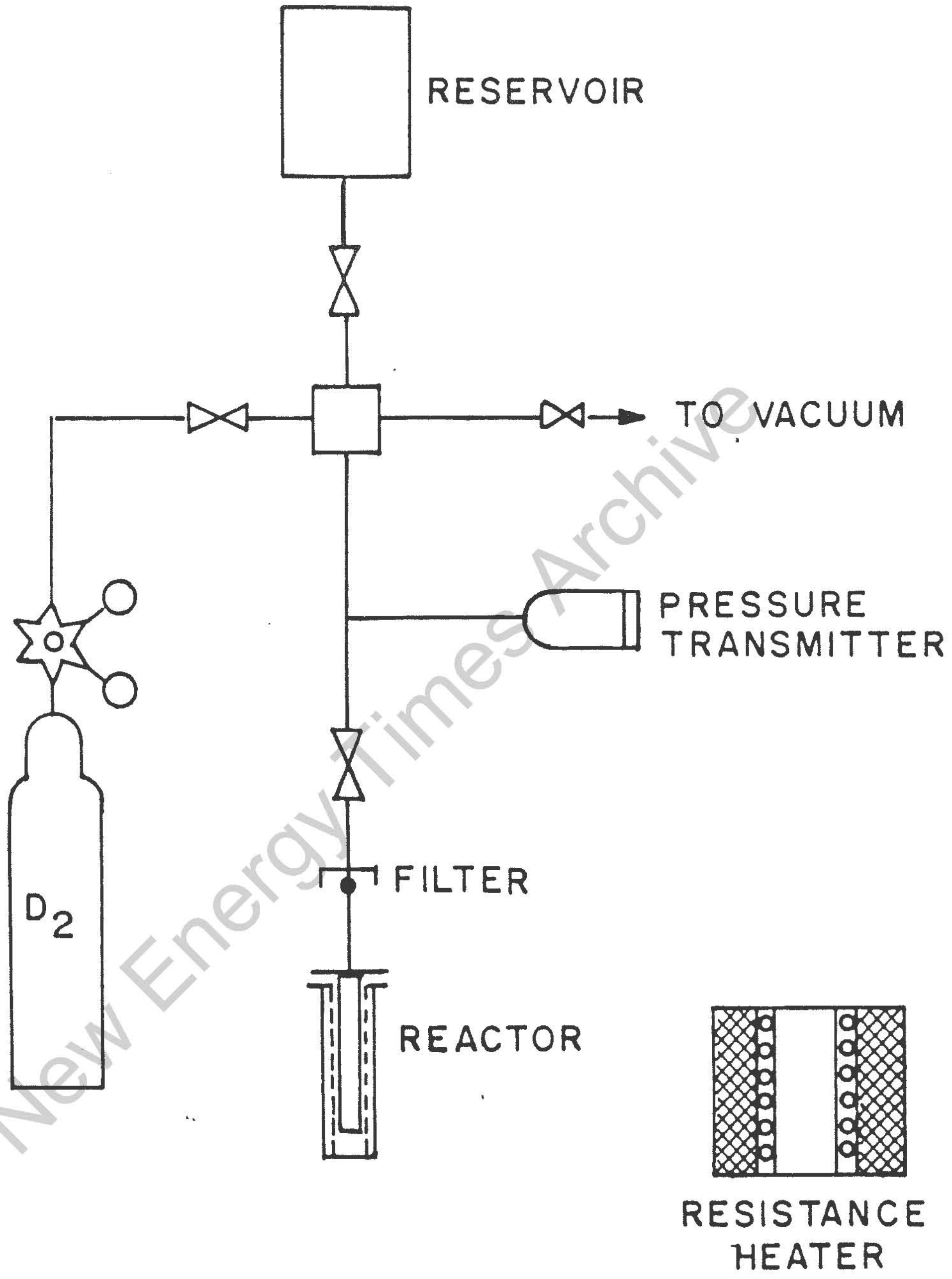

SCHEMATIC DIAGRAM OF THE
HYDRIDING / DEHYDRIDING UNIT

FIG. 1

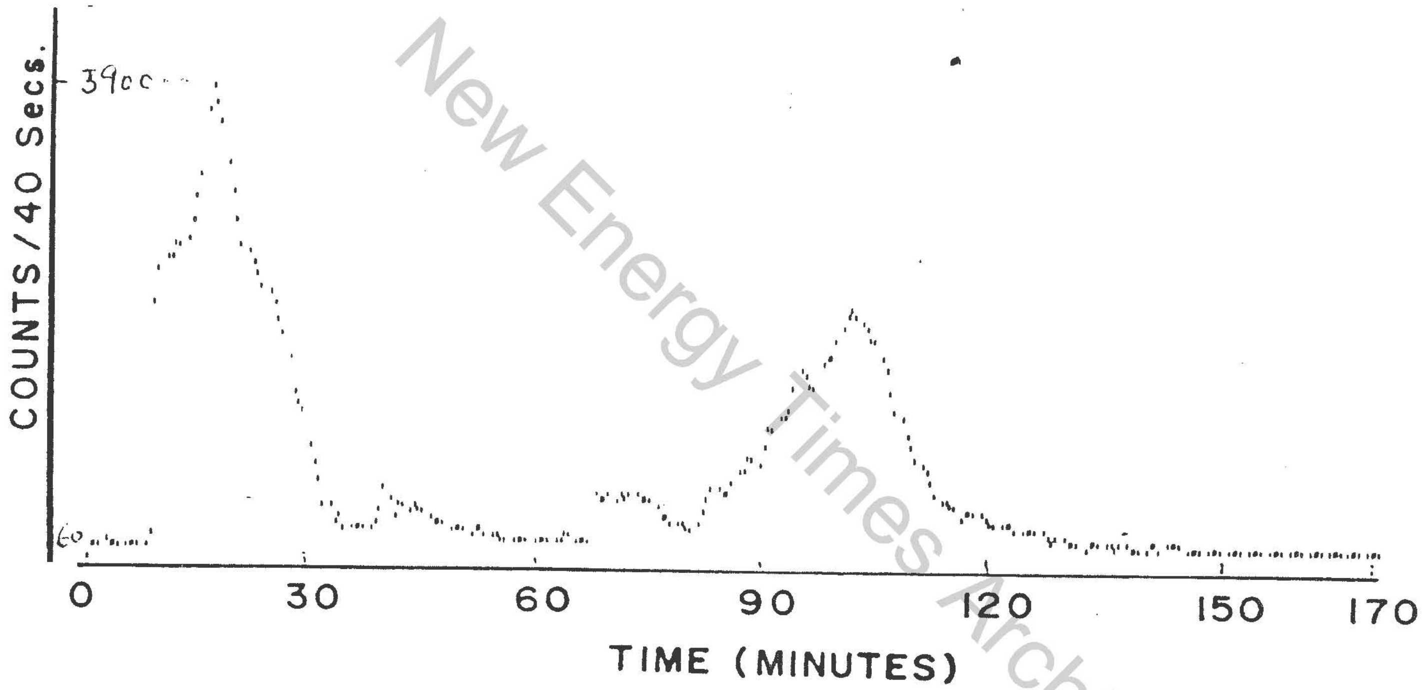

Fig.2 Desorption mode experiments (3rd June 1989)

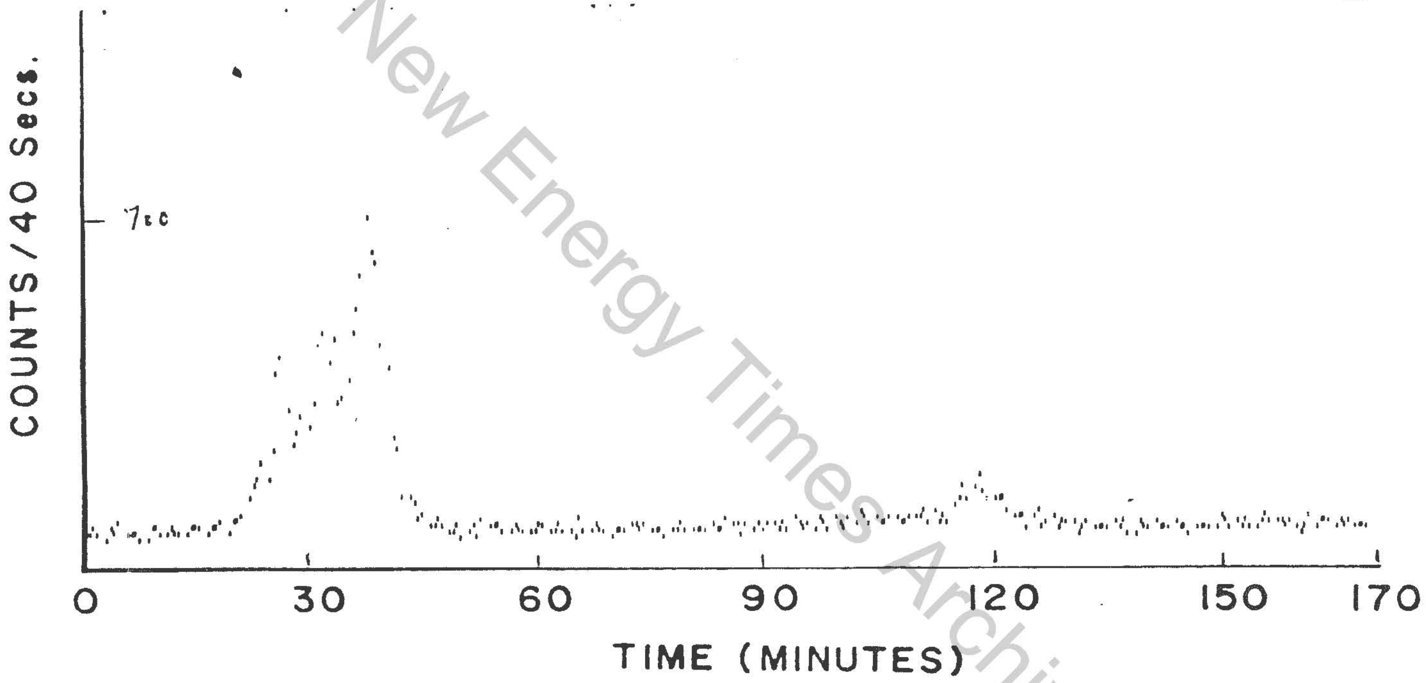

Fig.3 Desorption mode experiments (4th June 1989)

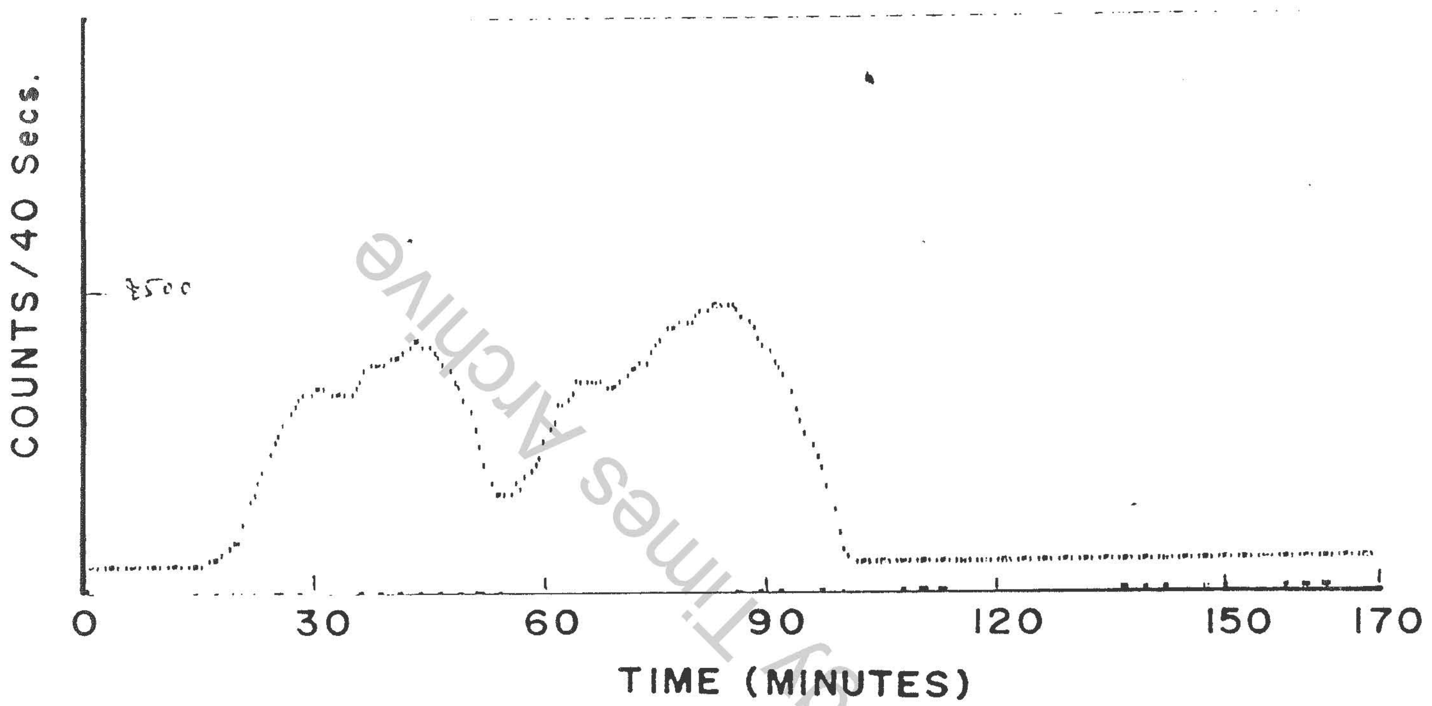

Fig.4 Desorption mode experiments after pressure cycling (7th June 1989)

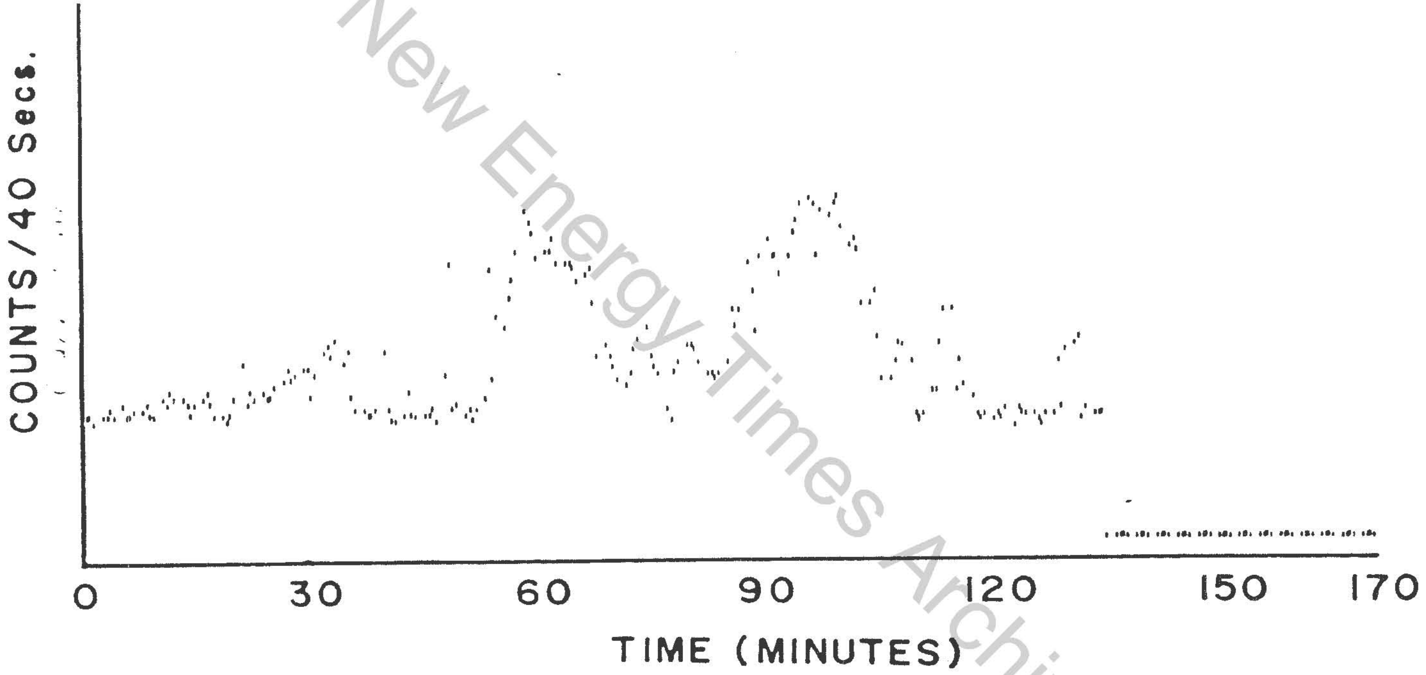

Fig.5 Desorption mode experiments after pressure cycling with second charge of Ti (17th June 1989)

Deuteration of Machined Titanium Targets for Cold Fusion Experiments

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Introduction :

Cold fusion experiments were conducted in solid targets made from titanium loaded with deuterium gas. The absorption of deuterium by Ti is a reversible process and when titanium is heated in a deuterium atmosphere, the reaction will continue until the concentration of deuterium in the metal attains an equilibrium value. This equilibrium value depends on the specimen temperature and the pressure of the surrounding deuterium atmosphere. Any imposed temperature or pressure change causes rejection or evolution of deuterium until new equilibrium state is achieved. If the surface of titanium is clean, the rate of absorption increases rapidly with temperature. At temperatures above 500 C, the equilibrium is achieved in a matter of few seconds and so deuteriation of targets can be achieved in a few seconds time. However, deuterium absorption is considerably reduced if the surface of Ti is contaminated with oxygen. Keeping in view these facts, a procedure was evolved for titanium target preparation and subsequent deuterium absorption. The following sections describe the details of preparation of the targets, chemical cleaning of the targets and degassing and deuteriation of the targets.

Preparation of the Targets :

Titanium targets of different sizes and shapes (planer, conical etc) were prepared. Targets were typically fraction of a gram in mass and were machined out of a Ti rod using Tungsten carbide tools with continuous cooling arrangement. Care was taken to avoid overheating during machining because any overheating hardens titanium and could spoil it.

Chemical Cleaning of the Targets :

Machined pieces were first degreased with acetone and then in an ultrasonic bath. Then the oxide layer was removed by immersing the sample in a 1:1:1 mixture of water, nitric acid and sulfuric acid. The targets were rinsed in water and acetone and then dried. HCl treatment was given to form an adherent hydride layer on the surface. Targets thus prepared can be preserved in a moisture free environment prior to deuterium absorption.

Degassing and Deuteriation of Targets :

Targets were first degassed by heating to ~900 C in a glass vacuum chamber using a 3kW, 2 MHz induction heater. Degassing was continued till a vacuum of less than 2 x 10^{-5} Torr was achieved. Targets were then heated to ~600 C in H_2 atmosphere at ~1 Torr pressure and allowed to cool. H_2 was released again by heating to 900 C. At least three cycles of H_2 absorption/desorption were given to create active sites for D_2 absorption.

After release of all H_2, the target was heated to 900 C in D_2 atmosphere at ~1 Torr pressure and allowed to cool by switching off the induction heater. D_2 gas was absorbed While cooling. At least three cycles of D_2 absorption/desorption were given similar to H_2 absorption/desorption. It was found that the absorption increased in each cycle and tended to saturate with 2nd or 3rd cycle.

Fall in pressure recorded by an oil manometer is a measure of the quantity of D_2 absorbed. It was noticed that each target could typically absorb ~1019 molecules of D_2. Considering that mass of Ti is a few hundred milligrams, this corresponds to an overall D/Ti ratio of <10–3 only. However, since most of the absorption is presumably on the surface, it is likely that the D_2 density is higher at the surface.

While preparing the targets, we found that their quality depends on various experimental factors. Some of them are listed here.
(i) Initial sandblasting of the targets for cleaning and roughening of the surface leads to better absorption of D.
(ii) Impurity content (such as O_2, N_2 etc) in D_2 should be $<0.1\%$.
(iii)Since the glass vacuum chamber is isolated from the pumping system during D_2 absorption, it is important that the vacuum chamber be leak tight. Small air leaks may contaminate the D_2.

Evidence for Production of Tritium via Cold Fusion in Deuterium Loaded Palladium

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After the first announcement reporting the observation of cold Fusion (1, 2) lot of evidence supporting the same have appeared in scientific literature and Press. Palladium an titanium loaded electrolytically (1,2) and titanium loaded directly with deuterium gas (3) have been reported to emit neutrons. However not many references have dealt with tritium measurement. Neither gas loading experiments involving Pd–D_2 nor tritium measurements in this have been reported. Experiments have been carried out in our group in the Pd–D system and tritium measurements in this system. The results obtained so far seen to strongly support the occurrence of Cold Fusion reaction.

EXPERIMENTAl

Preparation and pretreatment of Pd samples: For loading deuterium gas in Pd, two types of samples were used. One was Pd–Ag alloy supplied by M\s. Johnson–Mathey as directly used without further surface treatment. These were subjected to 600 c and vacuum of better than 10^{-5} mm or better for prolonged period, before use.The Pd black powder was prepared from $PdCl_2$.

Preparation of deuterium gas The D_2 gas used for gas loading as prepared from D_2O (supplied from production of HWP(B) and having a tritium activity of 0.075nci\ml) reducing with Na in a high vacuum system under stringent conditions. The gas produced gas is stored in a SS cylinder pressurising it with Activated charcoal liq N_2 cooling. The gas thus produced was not further analysed for tritium as it is expected to contain only 0.038nci\l activity.

Loading D_2 gas in metal phase: The schematic drawing of the experimental set up used for gas loading is given in Fig 1. It essentially consists of a vacuum system equipped with a rotary pump and an oil diffusion pump giving a vacuum of 10–6 torr. The reaction vessel C containing Pd sample is connected to the vacuum system through a buffer tank B . Deuterium cylinder D is connected to the vacuum system through needle valve V1. The entire system is of SS and tested for a vacuum of 10–6torr and pressure of 100Kg.cm–2. The system is also equipped with a pressure guage G and a manometer / pressure guage VG. A weighed amount Of Pd (black or metal) was taken in the vessel and heated to 600 C for 2 hrs. After cooling to room temperature, deuterium was filled at1 atm. pressure and allowed to attain equilibrium.

Preparation of Samples for Tritium Analysis: The vessel containing Pd sample was transferred into a closed glass container in a dry enclosure, free of moisture and O_2 and equilibration as kept at few hours to over night. This was necessary, as D_2 absorbed Pd samples hen exposed to moisture or O, is known to catalyse the recombination of absorbed D_2 gas with O_2, with considerable increase in temp. The entire deuterium absorbed is found to be desorbed through this step. Tritium counting –Liquid samples containing tritium were analysed in a liquid scintillation Spectrometer, for varying time and applying different corrections, as per procedures given in a separate paper else where in this Report. Autoradiography of the deuterium loaded samples. The experimental procedure for this investigation is described elsewhere in this report. It essentially consists in keeping. The gas loaded sample on negative Xray film and developing them after predetermined time

Results and discussion

As expected, absorbing of deuterium in pd–black as very fast and it readily gave a

stoichiometry of pd D 0.6 (as calculated by reduction in pressure of deuterium). But in case of the alloy the absorption as rather slow and also the amount of deuterium absorbed as much less than that corresponding to a bulk Pd D 0.6.u
As mentioned earlier we employed equilibration with distilled water for determination of tritium. This method was chosen for its simplicity and rapidity. Thy other possibility would had been to liberate the absorbed deuterium gas completely at 600° C and then either counting it directly in ionization chamber or oxidizing it to corresponding oxide and than analysing by liquid scintillation counting. But this becomes very impracticable because of the low amounts of gas absorbed (in the small amounts of metal samples taken) Taking into consideration the exchange reaction.

_Tabs + H2o = Habs + HTO ....(1) and applying law of mass action one obtains following relation for low tritium concentration :–
$Y_i.n_a = n_l[x_e(1/k + 1) - x_i]$....(2)
where x & Y refer to tritium atom fraction in the absorbed and the liquid phase respectively and subscripts i and e refer to initial and equilibration conditions respectively. na & nl are the gm moles of gas absorbed in metal & gm moles of water taken for equilibration
K is the equilibrium constant for reaction (1) and was taken to be same has for exchange of tritium between hydrogen and water, as after equilibrium the system consists mainly of H both in the absorbed and the liquid phase. The value of K is 6.128 at 30°C [Ref.4].
Yi calculated from equation gives the No of tritium atoms produced for every deuterium atom absorbed in the metal. The tritium atom fraction x can be calculated from the tritium activity A applying equation 3.

$$x\,o = \frac{1}{d \times 3320} .A \quad ....(3)$$

where A is activity in ci/ml and d is density of water in gm/ml.

(d = o.996542 at 27 oC)

The results of two typical experiments conducted are given in Table (1)

The samples of deuterium loaded metal were also subjected to autoradiography [Ref.6] for direct evidence of tritium. In case of Pd–black powder no fruitful conclusion could be drawn as the x–ray film got spoiled because of the powder sticking to the film. But in case of Pd–Aq soils it gave unmistakable fogging of x–ray film once again indicating the emission of some radiation from the foils

Unlike the Ti–tritium system the emission of Pd–Kα does not happen in the case of Pd–tritium system, as is known.

The Pd samples loaded with deuterium therefore did not show any thing (Ref.7). But one important observation made in this case where Pd foils ere loaded with deuterium after using the system for Titanium sponge. The titanium sponge, though had absorbed substantial amounts of deuterium (corresponding to Ti Du 1.7), had not shown any signature of tritium. But the Pd samples loaded subsequently in the same cell ere exhibiting Kα of Ti. The surface of the Pd foils was then found to be contaminated with Ti. This was another indirect proof of tritium having been produced in the Pd–deuterium system.

conclusions;–

There is a clear cut evidence for production of tritium in the Pd–D_2 system and they most plausible explanation appears to be fusion of two deuterons giving tritium.
The system did not require high pressure of D_2 gas also no special efforts ere made to creates no non–equilibrium conditions as suggested by De Ninnoetal (Ref). Although no comparison between the electrolytically loaded & gas–loaded Pd can be made as yet; electrolysis does not seen to be a necessary prerequisite for inducing cold fusion. However a comparison in terms of 'yield' of cold fusion and also the mechanism of cold fusion in the two system would be interesting. Unfortunately no so far neutron measurements have been carried out so far in the present work. A correlation between neutron production if any & tritium production would contributes significantly towards confirming the mechanism being cold fusion.

Acknowledgements :– Authors sincerely wish to express their gratefulness to Dr. P.K. Iyengar , Director, BARC for his keen interest and constant guidance in the present work. We are also thankful to Dr. M. Srinivasan for fruitful discussions. We also thank Dr. A Shyam and Mr. R.K. Raut for autoradiography and Dr. Madan Lal for the Si(Li) detector measurements.

Dr. T.S. Iyengar has carried out Tritium measurements described in this paper, which has been included elsewhere in this report. The authors would like to express their thanks to him.

Shri. V.H. Patil has been of great assistant in the experimental work. We thanking for same.

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TABLE 1

Summary of Results of Gas Loading Experiments in Palladium

Sl. No.	Sample	D/Pd Ratio	nl/na	Tritium activity of water used for equilibration, X_i	Tritium activity of water after equilibration	Y_i T/D ratio in metal
1.	Pd-black	0.63	46.96	1 pci me^{-1}	0.22 nci/ml	3.615×10^{-12}
2.	Pd-Ag foils	0.46	213.33	-do-	0.16 nci/ml	12.63×10^{-12} (1.263×10^{-11})

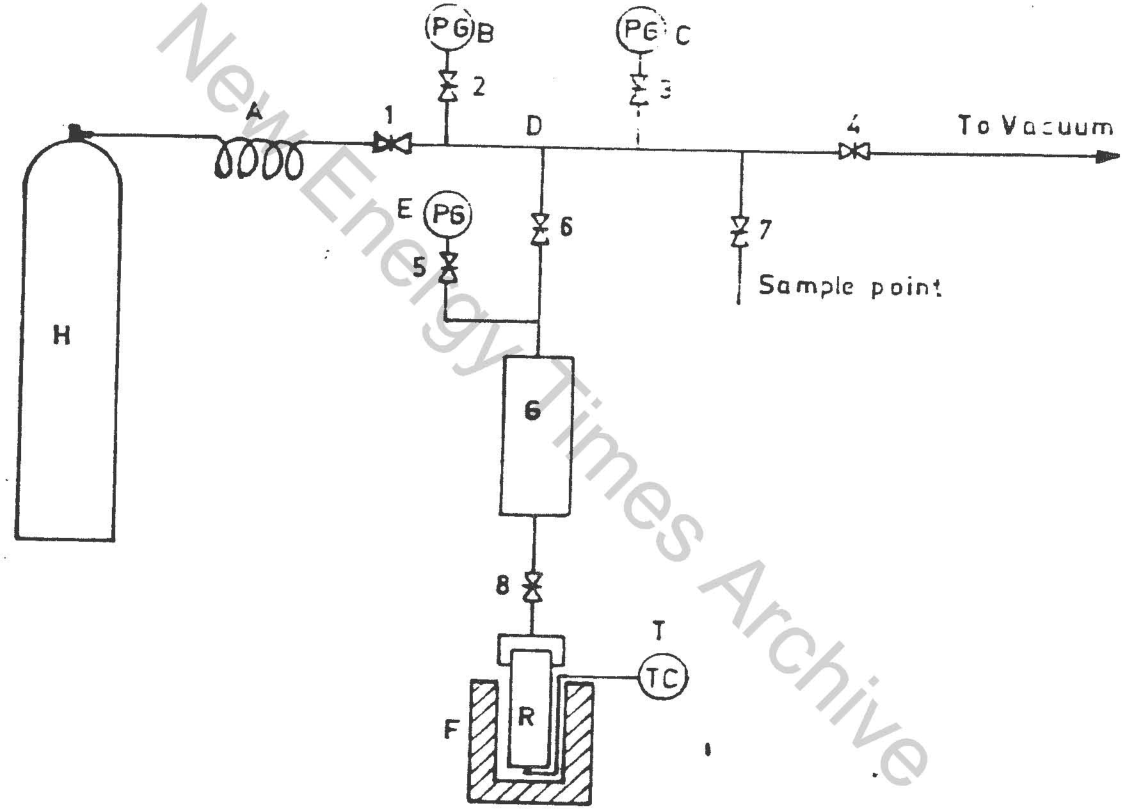

Fig.1. Schematic diagram of high pressure equilibration system

MATERIALS ISSUES IN THE SO CALLED "COLD FUSION" EXPERIMENTS

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In a recent electrochemical experiment with palladium cathode and platinum anode, immersed in 99.5% D_2O + 0.5% H_2O plus 0.1 M LiOD, M. Fleischmann and S. Pons[1] claimed to have seen an "excess heat" which they ascribed to "cold fusion" of deuterium nuclei electrochemically infused into the palladium lattice. These authors and Jones et al[2] have attempted detection of neutrons/H^3 as signatures of fusion based on the well known reactions:

$$D + D => He^3 + (0.82\ MeV) + n\ (2.45\ MeV),$$
$$D + D => H^3 + (1.01\ MeV) + p\ (3.02\ MeV),$$

and have found some favourable evidence. So far efforts to confirm their findings made in various laboratories, including BARC, have been somewhat inconclusive, although some neutrons appear to have been seen occasionally. The reported neutron production[1] is about six to nine orders of magnitude less than what the "excess heat" would imply. These observations have generated a great amount of debate[3] concerning the nuclear physics of D–D reaction; novel ideas have been proposed including the reaction $D + D => He^4$, with the added requirement that the energy (23.8 MeV) be delivered directly to the lattice. Even when they have been observed, often it has been claimed that neutrons appeared only intermittently. In view of these features we deem it prudent to draw attention to some of the relevant solid state aspects of Pd–D system which might be involved in some way.

Absorption of hydrogen/deuterium by Pd has been studied for a long time and is known[4] to be strongly exothermic. Neutron diffraction[5] experiment shows that H/D goes into the octahedral sites in Pd lattice. Accompanying this uptake is a structural change with the solid changing from the α phase at low H/D concentrations to $\alpha + \beta$ phase at higher values to an eventual β phase. Both the phases are f.c.c. with cell constants 3.89 A and 4.03 A respectively. Calorimetric studies[4], using activated Pd and molecular D[–]2[–] gas, show that at 30^0 C, the heat released during the formation of PdD_x, rises from ≈ 7.50 K Cals per mole of D_2 for $x \approx 0.023$ to ≈ 8.43 K Cals per mole of D_2 for $x \approx 0.422$, with the authors asserting that "these heats show a definite increase for each increment of gas added throughout the mixed phase region". Thus as more D atoms are loaded into Pd, one may expect that the β phase regions (with a higher lattice constant and presumably better cohesion) would grow in the matrix of α phase, leading to regions of localized strains. We may conjecture that eventually abrupt atomic readjustments may occur giving rise to conditions —such as local heating and energetic deuterium motions— that are relatively more favourable for some of the D–D fusion mechanisms proposed in the literature. This description also suggests that the results of the electrochemical experiments could be very much sample dependent.

Let us next turn to the enthalpy release. Actually there are several adsorption, absorption and desorption processes involved in the experiment using an electrochemical cell. But here we will concentrate only on the heat of formation of PdD_x, which has not received enough attention. We first note that in electrolysis, using Pd as a cathode because of its special ability to dissolve H/D, one generally does not observe any evolution of H_2/D_2 at the beginning, as these are absorbed by Pd. Also we may bear in mind that the values of the enthalpy release in the formation of PdD_x quoted above from ref. 4 relate to the situation with molecular D_2. If we were to measure these using nascent (i.e. atomic form) deuterium, then the enthalpy released would be larger by the dissociation energy[6] of D_2, viz 106 K Cals per mole of D_2. Assuming that the (cathodic) current in the Fleischmann – Pons experiment is only due to flow of D^+, we can then infer the amount of deuterium impinging on the Pd cathode and then roughly estimate the rate of enthalpy release due to deuteride formation. We estimate that it is of similar magnitude as the claimed "excess heat" by Fleischmann and Pons and emphasize the need to include it in the total energy balance calculations.

To sum up, we feel that the neutronic signals reported to have been seen in some of the recent electrochemical experiments deserve to be viewed in the light of the materials science of palladium deuteride. Although if it is finally confirmed this so called "cold fusion" would be physically very interesting, the possibility that it will lead to a significant new energy source appears doubtful at present.

We acknowledge helpful discussions with a large number of colleagues especially Dr. P. K. Iyengar, Dr. S. Gangadharan, Dr. T. P. Radhakrishnan and Dr. S. K. Sikka.

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RCBowman

MATERIALS CHARACTERIZATION SECTION

Relatively little emphasis has been placed on the role of materials in "cold fusion" experiments and generally characterization of the anode and cathode materials has not played a significant role in the discussions. Most experiments have utilized Pd cathodes for the electrolytic charging and Ti (or Ti alloys) for gas charging experiments following the examples of the initial experiments by Pons, Fleishmann, and Jones. In addition, most electrolysis experiments have utilized Pt anodes, with the important exception of those at Texas A&M which are reporting ^3H generation and which utilize Ni anodes.

It has become increasingly common for the D/Pd ratio attained to be reported in the electrolysis experiments with the measurements generally being based on the weight gain of the cathode. Values of D/Pd in the range 0.7 to 1.1 have been commonly reported for experiments with both positive and negative "cold fusion" results. The gravimetric method of measurement is generally relatively reliable for D/Pd values in the range of 0.6 to 1 as long as the loss of D is minimized between the period of charging and the weighing. Most investigators do not report the details of their procedures, such as the storage of specimens at low temperature to avoid this problem. An additional difficulty in these experiments is that many investigations report deposits on the cathode or diffusion of Li into the cathode and these must be removed before weighing to determine the D/Pd values. It does not appear that this has been done.

In a number of cases the cathodes have been analyzed for ^3H, ^3He, and ^4He with negative results. Reports of diffusion of Li into the cathodes have been made but the bases for these reports have generally not been specified. In one case the presence of Li up to several micrometers into the Pd cathode was detected by SIMS measurements but the authors suggest that this was the result of surface cracking and contamination of the crack surfaces by the electrolyte. They also detected other components of the electrolyte in the cathode by the same technique.

Even less characterization of the materials has been carried out for the gas charging experiments. Often mixtures of metals have been used and they have been characterized as "turnings", "sintered powder", "mossy solids" etc. none of which have any meaning with respect to the materials character. The D/Pd ratios have not been determined nor has sufficient information been given to even allow an estimate to be made. This is particularly true as the absorption of D in Ti and its alloys is a very surface sensitive process.

As discussions of the success or failure of "cold fusion" experiments have often been ascribed to properties of the cathode materials it is useful consider the various parameters suggested to be important in light of what is known of the behavior of D(H) in Pd and Ti.

a. Success of the electrolytic experiments has been ascribed to the very high "confinement pressures" achieved at the overpotentials applied. As discussed in Appendix -- the overpotential results in a very high fugacity of D at the Pd surface but this corresponds to a much lower pressure due to the non-ideality of D_2 gas and to the loss of D_2 by gas formation at the surface. The compositions attained by cathodic charging correspond to a very moderate pressure of 15 kbars. -- 15,000 atmospheres or 220,000 ~~[illegible]~~ pounds per square inch.

Double 2

b. The suggestion has been made that as a result of the high fugacity, confinement of D in Pd results in a very small D-D distance. As discussed in Appendix -- the smallest distances between interstitial sites occupied by D in Pd is 0.151nm which is ~~large compared~~ ~~to~~ the D-D distance in the D_2 molecule. Significant dual occupancy of interstitial sites by D is not in accord with the linearity of the lattice expansion measured by x-rays or with theoretical treatments of the Pd-D system; simulations show that dual occupancy will still yield average separations larger than that in a D_2 gas molecule.

c. The suggestion has been made that successful experiments require very long charging times. As discussed in Appendix -- the diffusivity of D in Pd is sufficiently large at 300 K so that equilibrium can be attained in a 1 cm thick sheet of Pd in times of the order of hours.

d. A suggestion that a particular form of the cathode material, e.g.. cast material, must be used to minimize the dislocation concentration is not in accord with known behavior of Pd as discussed in Appendix --. The very large inhomogeneous deformations which accompany cathodic charging of Pd under the conditions used result in high dislocation densities even in a well annealed material. Thus regardless of the initial starting point, the charging conditions result in severe deformation of the cathode.

e. Deposition of various materials from the anode and from the electrolyte (leached from the container) on to the cathode has clearly occurred in many of the experiments. Analysis has revealed Pt (probably from the anode), Si (probably leached from the glass container), Cu, Zn, Fe, Pb, and other trace elements. The surface contamination may affect the rates of reactions at the cathode surface and therefore the effective fugacity. In general surface poisons increase the fugacity by decreasing the rate of D_2 formation. This is indicated by the high D/Pd values attained and by the observation, reported in several experiments, that the loss of D from the cathode after electrolysis was slow. Thus surface contamination probably had the effect of increasing the D/Pd values and the fugacities attained. "Dendritic" growths were reported on the surfaces of the cathodes in the Texas A&M experiments which utilized Ni anodes. This has lead to the suggestion that these dendrites are of significance, possibly due to increased electric fields at the "dendrite" tips, in the formation of ^3H in the electrolyte. Other experiments which reported these "dendrites" have not reported generation of ^3H. It is difficult to understand the importance of these "dendrites" particularly as these growths are not uncommon in plating experiments. The suggestion that ions of kilovolt energy can be created as a result of the action of ~~the~~ dendrites is incorrect.

APPENDIX --: MATERIALS FOR COLD FUSION

A. The Palladium - Hydrogen (Deuterium) System

"Cold fusion" experiments have utilized two types of cathode materials; palladium and titanium (including several titanium alloys). These two metals have significantly different behaviors in the presence of hydrogen and its isotopes. Their response to exposure to hydrogen isotopes has been extensively studied and well documented[1,2]; particularly in the case of palladium. In the following, we shall highlight some of the behavior of the Pd-H and the Ti-H systems selecting those aspects which are most pertinent to the issues raised by the suggested "cold fusion" experiments. Much of what is known derives from experiments using the mass one isotope, ^{1}H (also denoted by H), but studies have sufficiently established the isotopic dependence to allow the behavior of deuterium, ^{2}H (also denoted by D), to be deduced where measurements on D are not available. Many aspects of the behavior of hydrogen isotopes in bcc and fcc (Pd) metals have been clearly shown[1] to be dominated by their behavior as quantized particles; other properties can be understood using classical concepts. Behavior as quantized particles has not been established for hydrogen isotopes in the hcp crystal structure (titanium) but such behavior may be expected.

Palladium has a face centered cubic (fcc) close packed crystal structure and as hydrogen is added this structure is maintained across the phase diagram[3]. It can absorb large quantities of H(D) with concentrations as high as H/Pd = 1.1 being attainable. The H(D) occupies predominantly octahedral interstitial sites which if they were all filled would result in a H(D)/Pd ratio of 1. Hydrogen can also be accommodated in tetrahedral interstitial sites at a somewhat higher energy and it is believed that these sites may be partially occupied at the higher H(D)/Pd ratios. The spacing of H(D) occupying these sites is not particularly small as shown by the table below. Both the octahedral and tetrahedral sites have cubic site symmetry and since H(D) appears to have random occupancy in the occupied sites the maintenance of cubic crystal structure is consistent with the high H(D)/Pd values attained. Further evidence for the random occupancy of sites and the cubic distortion of the lattice is provided by x-ray studies of the Pd-H(D) system[4] which also indicate that the behavior of D is closely similar to that of H. Recent theoretical treatments[5,6] of the behavior of H(D) in

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DEUTERIUM - DEUTERIUM DISTANCES

SITES OCCUPIED	DISTANCE IN NANOMETERS
nearest neighbor octahedral sites	0.151 ?
nearest neighbor tetrahedral sites	0.275
nearest neighbor octahedral - tetrahedral sites	0.168
vacancy sites	0.185
molecular deuterium gas	0.074
liquid deuterium	0.27 (but also 0.074)
water	0.151

Pd are consistent with the conclusion that H(D) does not attain exceptionally close nearest neighbor distances even under dynamic conditions. Molecular dynamic simulations[5] at concentrations up to D/Pd = 1.1 found no D-D distances shorter than 0.07 nm compared to the molecular D-D distance of 0.074 nm. Interactions of D with lattice defects have been studied both experimentally and theoretically. Significant attractive interaction energies are found[7] with those defects which have a decreased electron density such as vacancies. Palladium has such an attractive interaction but it is particularly weak. Each vacancy can accommodate up to 6 D interstitials with the D solutes occupying sites displaced towards the octahedral interstitial sites adjacent to the vacancy. The D-D distance is 0.185 nm.

The phase diagram of the Pd-H(D) system[2,3] is typical of that of many of the bcc and fcc hydride forming systems. The dominant feature is a miscibility gap with a critical temperature of about 549 K and a critical composition of H(D)/Pd ≈ 0.27. At about 300 K the initial α phase has a solubility of about H/Pd ≈ 0.03 and the two phase region extends to about H/Pd ≈ 0.65 at which point the β is formed. Both the α and β phases have fcc structures. Phase relations in the Pd - H system depend on the isotope of hydrogen used but the differences are not very large. Important differences exist in the P-C-T data[2,3] which characterize the equilibrium of gaseous hydrogen isotopes with Pd but these differences are consistent with the differences in the isotopic masses. Many of the thermodynamic properties of the Pd - H(D) system are consistent with theoretical calculations based on mean field theory[8] which is based on a repulsive nearest neighbor interaction between H solutes. This repulsive interaction has been measured using a variety of methods[7,9,10,11]

While the α and β phases are solid solutions of H(D) in the Pd interstitial sites, formation of long range ordered structures does occur at high concentrations and low temperatures[12]. These structures form by the ordering of the H(D) interstitials on subsets of the interstitial sites and are consistent with the nearest neighbor repulsive interactions between the H(D) interstitials. At H(D)/Pd = 1 the structure is of course ordered if the H(D) occupies octahedral interstitial sites. No other hydrides are known to form at temperatures of the order of 300 K in the high concentration region of the phase diagram although few careful investigations have been carried out in this region. The lattice parameter measurements[4] which extend into this composition region indicate a quite linear lattice expansion up to H/Pd = 1.0.

~~Similar to that of~~ [illegible]

Hydrogen and its isotopes diffuse very rapidly in the Pd lattice[8]; at 300 K the diffusivity of H in the α phase is about 2x10^{-9} m^{2}s^{-1}. The diffusivity in the β phase is somewhat slower but is still very high. The effect of isotopic mass on diffusivity is very non-classical in Pd with the $D_D > D_H > D_T$ at 300 K; a clear indication of the quantum mechanical tunneling process which dominates the diffusion of H(D) in the Pd lattice. With respect to the "cold fusion" experiments an important point is that with the known diffusivities of D in Pd, a time of the order of 3.5 hrs. is required to achieve equilibrium during the charging of a 1 cm thick sheet specimen. [illegible]

Hydrogen charging of Pd can be carried out in several ways. Electrolytic charging with the Pd as a cathode has been carried out in a number of different electrolytes. In general, the Pd surface is highly active towards the dissociation of the H_2 (D_2) molecule and hence little H_2 (D_2) gas is evolved until relatively H(D)/Pd ratios are obtained at which point the back diffusion of H(D) to the surface becomes significant. Additions of "poisons" such as As ions to the electrolyte increase the fugacity of the H(D) at the surface by decreasing the formation rate of H_2 (D_2) and hence allow a higher H(D)/Pd value to be obtained with the same overpotential. Since the fugacity of hydrogen depends on the overvoltage as well as on the surface conditions it is difficult to obtain a direct relation between the cathodic charging conditions and the H(D)/Pd values obtained. Since H_2 (D_2) is a highly non-ideal gas, at high fugacities the equivalent pressures are many orders of magnitude less than the fugacities.

Gaseous charging of hydrogen is also commonly carried out[13] and high H(D)/Pd ratios can be obtained for relatively moderate pressures. Solution of H(D) in Pd follows Sieverts law at low pressures and then shows significant deviations from ideal solution behavior, probably as a result of H(D) - H(D) interactions in the Pd. In the region of Sieverts Law behavior the proportionality of the H/Pd to the $P_{H_2}{}^{1/2}$ is further evidence for solution of H(D) in Pd in the atomic form rather than as a molecule.

Concentrations of D/Pd ≈ 1 are often attained in "cold fusion" experiments and are often quoted as a necessary condition. It has also been suggested that the "very high confinement pressures produced by electrolytic charging" are necessary for "cold fusion". Comparison of the results of gaseous charging with electrolytic charging allows an estimate of these "confinement pressures" to be made. A concentration of about D/Pd ≈ 1 requires a gas pressure of about 15 k bars at 300 K[12]. Thus the effective pressure corresponding to the high fugacities calculated from the overvoltages during cathodic charging are equivalent to a very moderate pressure indeed.

Palladium is an "exothermic occluder" of H(D), i.e. the heat of solution relative to the gas phase as a standard state is negative. The heat of solution is relatively small having a value of -19 kJ/mole H_2 in the α phase[2,3] a value of about -46 kJ/mole H_2 in the β phase[11]. Values for the heats of formation of the hydrides in the Pd - H(D) system have not been measured but most hydrides have heats of formation in the range -58 to - 209 kJ/mole H_2[2].

Formation of the β phase from the α phase during charging causes a large amount of lattice strain and deformation as the phase change is accompanied by a large increase in volume. Since the molal volume of the β phase is larger than that of the α, the β phase is in compression during charging. Correspondingly, the plastic deformation of the α phase during charging coupled with the decrease of volume during loss of hydrogen during the β to α phase change causes very high tensile stresses at the surface during the loss of hydrogen. The net result is significant plastic deformation during charging and deformation and fracture during loss of H(D).

B. The Titanium - Hydrogen (Deuterium) System

While considerably less is known about the Ti - H(D) system than about the Pd - H(D), our knowledge is sufficient to answer many of the questions of interest for the "cold fusion" experiments. At about 300 K hcp titanium absorbs H(D) in the α solid solution up to concentrations of about H(D)/Ti ≈ 0.05 although low temperature measurements are not very accurate due to the difficulty in absorbing H(D) from the gas phase at low temperatures. Above this concentration a two phase equilibrium exists between the hcp α solid solution and the γ hydride. This hydride exists over the composition range $\mathrm{TiH(D)}_{1.9}$

to $TiH(D)_2$ having a flourite fcc structure at the lower compositions and a face centered tetragonal structure as the H(D) concentration is increased. At temperatures above about 570 K H(D) solubility is about H(D)/Ti ≈ 0.1 and the solid solution is in equilibrium with the bcc β phase of Ti which is stabilized by H(D). The phase has a very high solubility for H(D) of the order of H(D)/Ti ≈ 1. Above this composition a two phase region exists where the β phase is in equilibrium with the γ dihydride, TiH(D)2. Since the β phase of Ti can be stabilized by many other solute additions, it is possible to absorb large quantities of H(D) into the β stabilized alloys at 300 K without forming hydrides. The extent of this low temperature solubility in the β stabilized alloys has not been established.

Site location studies have not been carried out for the Ti - H(D) alloys. Random occupancy of tetrahedral sites in the non-stochiometric γ hydrides was deduced from NMR measurements[14]. No information is available for site occupancy in the α and the β phases. If we assume tetrahedral site occupancy in the hcp α phase and both octahedral and tetrahedral site occupancy in the β phase the nearest neighbor distances given in the table below can be calculated.

DEUTERIUM - DEUTERIUM DISTANCES IN TITANIUM

α PHASE (HCP)	D - D Distance in nm
nearest neighbor tetrahedral sites	0.23
γ PHASE (FCC)	
nearest neighbor octahedral sites	0.22
β PHASE (BCC)	
nearest neighbor octahedral sites	0.17
nearest neighbor octahedral-tetrahedral sites	0.083

The thermodynamics of the Ti - H(D) system has been extensively studied. Formation of solid solutions of H(D) in the α and the β phases are exothermic as is the formation of the γ hydride. Differences of these values between H and D are very small. These enthalpies are given in the table below[2,15,16,17,18,19].

Measurements of diffusivity of H(D) in Ti have not been carried out but the diffusivity at 300 K can be deduced from permeation experiments to be about $1x10^{-10}$ m^2s^{-1}. This diffusivity would allow equilibration of a 1 mm thick sheet with a $H_2(D_2)$ atmosphere in

ENTHALPIES OF SOLUTION AND FORMATION
(kJ / mole H2)

	HYDROGEN	DEUTERIUM
solution in α phase	-90.4	-94.6
solution in β phase	-116.4	
formation of γ phase	-138	-121

0.7 hrs. Diffusion or permeation experiments are difficult to perform at low temperatures due to the presence of surface oxides on the titanium which inhibits the entrance of H(D) from the gas phase. Equilibration of Ti with gaseous H_2 is slow due to surface oxide. Even under cathodic charging conditions entry of H(D) is inhibited unless the surface oxide is minimized and "electrolytic" poisons used. As a consequence equilibration in a gaseous atmosphere or under cathodic charging is dominated by surface reactions.

Titanium hydrides are brittle and undergo cleavage when stressed. They serve to embrittle Ti and its alloys, causing materials which are only partially hydrided to powder. The introduction of H(D) causes a large volume increase as a result of the molal volume of solution (about 0.28 of the Ti atomic volume). In addition, formation of the hydride causes a volume increase of about 23% as a consequence of the difference in H(D)/Ti values for the α and γ phases and the volume increase accompanying the crystal structure change. It is not surprising that the gas charging "cold fusion" experiments report fracturing of the Ti specimens used.

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